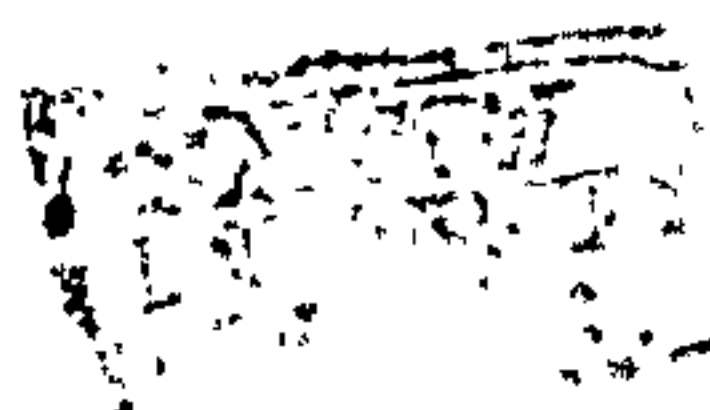


**The sedimentation and provenance of the Lower Old Red
Sandstone Greywacke Conglomerate, southern Midland
Valley, Scotland**

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This thesis is dedicated to my family:-my mother, Dotty;
my father, Charles; my sisters, Niki and Robin, and Paul.
Thank you for being so patient .

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Summary

The origin of the southern Midland Valley Old Red Sandstone Conglomerates is reviewed with the specific aim of determining the nature and location of the source for the Old Red Sandstone Greywacke Conglomerate. The Silurian Midland Valley has been viewed as either i). a fore-arc basin with a rising trench-slope basin to the south (Leggett, 1980, Leggett *et al.* 1983) or ii). an inter-arc basin with an arc in the Midland Valley and south in the location of the present day Southern Uplands (Bluck, 1983). The deposition of the Greywacke Conglomerate would thus record either the: i). culmination of a rising fore-arc and accretionary prism (Leeder *et al.* 1983), ii). time of emplacement between the northern section of the Southern Uplands and the Midland Valley (Thirlwall, 1988), or iii). age of the emplacement of the Southern Uplands over a missing fore-arc along a northward thrust, (Bluck, 1983). All of these models are dependent on the drainage basin for the Midland Valley within the present day Southern Uplands during Old Red Sandstone times.

A re-appraisal of the sedimentology of the Greywacke Conglomerate has shown the sequence is characterised by vertically stacked small ($\leq 2\text{km}$) proximal alluvial fan sediments deposited in a series of separate N-S trending basins, each with one dominant fault controlled margin towards the east. The geometry and sedimentation pattern of these basins suggest the Southern Uplands Fault could not have controlled deposition of the Greywacke Conglomerate.

The petrography and geochemistry of the greywacke clasts cannot be easily matched with a source in the Southern Uplands. The Southern Uplands sediments are characterised by petrographic consistency along strike. In contrast, there is a change in clast composition from the SW to the NE in the Midland Valley clasts, *i.e.* in the same general trend as the strike of the Southern Uplands.

The evidence indicates that the source for the Greywacke Conglomerate was a basement cover of greywacke within the Midland Valley. This source may have been accreted to the Midland Valley during or prior to the obduction phase of the Ballantrae ophiolite. The source probably formed a series of highlands within the Midland Valley block since the Wenlock with major uplift of this source occurring in the uppermost Silurian-(?)Early Devonian.

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1.0 Geotectonic framework of central Scotland

Three main structural blocks are recognised in Scotland, the Northwest Highlands, the Midland Valley and the Southern Uplands. The Midland Valley forms a belt of lowlands in central Scotland which is bounded by Caledonian-trending NE-SW faults. The Valley is terminated along the southern margin by the Southern Uplands Fault and along the northern margin by the Highland Boundary Fault. These faults mark major discontinuities separating the Dalradian block north of the Highland Boundary Fault and the Southern Uplands block south of the Southern Uplands Fault from the Midland Valley. The closure of an oceanic basin during Lower Palaeozoic times, the Appalachian-Caledonian Orogeny, resulted in the present disposition of different tectono-stratigraphic elements. The argument is therefore one of how these blocks or 'terrane' were brought together during the Caledonian Orogeny and what interpretation is given to them.

1.1 Evidence for destructive margin.

Palaeontological (Cocks and Fortey, 1982, and references therein) and palaeomagnetic evidence (Briden *et al.* 1984; Briden *et al.* 1988) confirm the 'Iapetus Ocean' separated the Laurentian continent (North America, Northern Britain, Greenland, eastern Newfoundland and western Norway) at equatorial latitudes from both the Gondwanan continent (Armorica, Iberia, Bohemia, Africa, eastern Newfoundland, and southern Britain) at high southerly latitudes and the Baltic continent (most of Scandinavia, the Russian platform and Poland) at temperate latitudes. The evidence suggests this ocean was possibly 1000 km wide during the Early to Mid-Ordovician times.

The Southern Uplands block is composed of a series of fault bounded sedimentary packages. Three major belts were recognized by Peach and Horne (1899) based mainly on the age of the sediments. The Northern Belt comprises Ordovician rocks of Caradoc to (?) Ashgill whereas the Central and Southern Belts are mainly Silurian in age. The boundary between the northern Ordovician rocks and the southern Silurian rocks is commonly taken as the trace of the Kingledores Fault (Fig. 1.1). The boundary between the Central belt and Southern belt, the Riccarton Line, was originally thought to divide Wenlock rocks in the southern belt from mainly Llandovery age rocks in the Central belt. It is now known that Llandovery and Wenlock occur on both sides of the Riccarton Line.

Within each belt a number of strike-slip fault bounded stratigraphical units are recognized (McKerrow *et al.* 1977; Leggett *et al.* 1979). The tracts are characterized by basal lavas, cherts, or graptolitic shales passing upward into thick turbiditic greywackes, some with conglomeratic horizons. Petrographically the greywackes show a progressive

change from quartz-poor, basic-igneous rich sandstones in the Ordovician to quartz and acid-igneous rich sandstones in the Silurian. Each tract youngs to the north and is in contrast with the overall Southern Uplands assemblage which youngs to the south.

The sediments throughout the Southern Uplands region contain deep-water clastics deposited from point sources in submarine fans as well as debris and axial wedge deposits (Kelling *et al.* 1987; Leggett, 1980). The conglomeratic horizons have been interpreted as submarine canyon and fan-channel deposits (Kelling and Holroyd, 1978). It was the structural arrangement and the interpretation of the rocks as ocean floor and trench sediments which led Mitchell and McKerrow (1975) to interpret the Southern Uplands as an accretionary prism formed along the southern margin of the Laurentian continent during closure of the oceanic basin.

Leggett (1980), Leggett *et al.* (1983), Yardley *et al.* (1982), Leeder (1982) view the structural elements of the Scottish Caledonides during the Ordovician-Silurian as :

- i). a frontal metamorphic arc located in the Grampian Highlands
- ii). A magmatic arc represented by volcanics in the Midland Valley and Grampian Highlands and 490 Ma. gabbros and associated rocks in the Aberdeenshire Grampians
- iii). A fore-arc basin occupying the southern and central regions of the Midland Valley and
- iv). An accretionary prism represented by the Southern Uplands.

Using this model there need not have been any substantial lateral or compressional movement along the boundary faults.

1.2 Evidence for terrane accretion.

The recognition that Scotland lay on the southern destructive margin of Laurentia was followed by the concept of terrane accretion. It is suggested that the southern Highlands, Highland Border Complex, Midland Valley, Ordovician sequence at Girvan, Ballantrae Complex and Southern Uplands comprise 6 terranes (Fig. 1.1), each with an individual history and each accreting to the southern margin of Laurentia at different times. A possible seventh terrane is suggested by Anderson and Oliver (1986) where they recognize that the Orlock Bridge Fault may subdivide the Southern Uplands into two individual terranes.

The Dalradian block is mainly composed of Late Precambrian to Cambrian sedimentary shelf deposits metamorphosed during the Grampian Orogeny, 510-490 Ma. Recent investigation of the Highland Border Complex, a sequence of serpentinites and sedimentary rocks just south of the Highland Boundary Fault, indicate it was formed in an intra-oceanic marginal basin which separated the Dalradian block from the Midland Valley block in Early Ordovician times (Curry *et al.* 1984; Bluck, 1985; Robertson and Henderson, 1984).

Uplift ages for the Dalradian, c. 520-420 Ma, record the removal of a substantial thickness of metamorphic detritus, 15-25 km, which is thought to have been dispersed southwards (Watson, 1984; Bluck and Leake, 1986; Watson, 1985). A large portion of this material which should have entered the adjacent Midland Valley is absent with only minor metamorphic clasts found in the Highland Border Complex of disputed Dalradian origin. The juxtaposition of the Scottish Dalradian block next to the Highland Border Complex was probably achieved by a major strike-slip event (Robertson and Henderson, 1984; Harte *et al.* 1984).

Geochemical evidence from the granitic and associated rocks in the Dalradian block have also been used to support the theory of an early-middle Ordovician separation between the two blocks. The main structural and metamorphic events of the Dalradian Supergroup, the Grampian Orogeny, took place between 500-530 Ma. Syn- and pre-tectonic granites, c. 540-430 Ma., do not have a subduction related genetic inheritance (Clayburn, 1981 in Leggett, 1983) and are considerably younger than unfoliated granite clasts, c. 560 Ma., from the Midland Valley Ordovician Benan Conglomerate near Girvan. The existence of Early Cambrian granitic clasts and their association with metaquartzites and mica-schists which do not bear any resemblance to the Dalradian indicates that a crystalline crust considerably older than the Dalradian existed in or adjacent to the Midland Valley.

The oldest rocks exposed in the Midland Valley are located along the southern margin in the southwest corner near Girvan, the Ballantrae Complex and the Ordovician sedimentary sequence. The Ballantrae Ophiolite Complex, a structurally complex sequence of serpentinised ultramafics with minor intrusions associated with cherts, shales, pillow lavas and volcanogenic products, is located north of the Stinchar Valley Fault and is Early Arenig in age (Hamilton *et al.* 1984). The Ballantrae Ophiolite has been regarded as an oceanic slice formed in a marginal basin (Bluck *et al.* 1980a; Thirlwall and Bluck, 1984) a slice of oceanic crust (Leggett *et al.* 1982) or the remnant of an oceanic edifice (McKerrow, 1982; Barrett *et al.* 1982). The complex was obducted by the Middle Ordovician, at 478 ± 4 Ma (Bluck *et al.* 1980a) along a northward dipping subduction zone.

The majority of the Ordovician sediments are located between the Stinchar Valley Fault and the Glen App Fault further south, although it is not clear which of these faults is the westerly equivalent of the Southern Uplands Fault. The Ordovician sedimentary sequence is divided by the Stinchar Valley Fault into relatively thick coarse conglomerates, sandstones and shallow water reefal limestones to the north and thinner deeper water turbidites, collectively known as the Tappins Group, to the south. The sediments range in age from Upper Llanvirn to Ashgill and overstep onto the Ballantrae Ophiolite (Ingham, 1978).

The Ballantrae Ophiolite Complex thus formed part of the basement across which the later Middle Ordovician sequence made a northwestward transgression.

The structure and depositional history of the middle Ordovician was described by Williams (1962). He showed the Middle Ordovician sediments were deposited in a number of basins which had active faults on their northwestern margins where thick conglomerates derived from the northwest pass laterally into axially derived sediments in the southeast. The sedimentology of the northwestern margin of these basins was dominated by submarine fans (Bluck, 1983) and fan deltas (Ince, 1984) whereas axially derived turbiditic sandstones and mudstones towards the south were accumulating in deep water. The same overall trend continued into Late Ordovician times (Ingham, *ibid*).

The composition of the Ordovician conglomerates near Girvan has been studied by Bluck (*ibid*). The conglomerates; Kirkland (Llanvirm), Benan (Llandeilo), and Kilranny (Caradoc) all have a similar composition. However, comparison of the three conglomerates reveal significant variations in the percentage of the constituents.

In the oldest conglomerate the majority of the clasts are basic to ultramafic. The composition of the mafic igneous fragments in the conglomerates vary from a direct association with the Ballantrae Igneous Complex to rocks which do not show any clear affinity with the Complex. The remaining constituents found in the conglomerate include granitic, dioritic, porphyritic and metamorphic compositions. Granitic debris becomes progressively more abundant in the Benan through Kilranny conglomerates at the expense of mafic detritus. The granitic fragments dominate the coarser grained fraction in the younger conglomerates especially in the Kilranny conglomerate with granitic clasts in excess of 50 cm. There is also a progressive appearance of acidic hypabyssal rocks upward through the conglomerate sequence. This change from a mafic rich source to a acidic source in the Ordovician succession is mimicked in the finer-grained sediments of the Tappins Group which have abundant detrital serpentine and mafics in the lowest sandstones with progressive quartz enrichment in the upper sandstones.

The granitic boulders have been dated by Longman *et al.* (1979) and range from c. 590 to c. 450 Ma, the youngest clasts dated in each conglomerate having a similar age to the base of the formation in which they occur. This implies that the parent plutons were uplifted and eroded not long after they were formed.

Bluck (1983; 1985) has suggested that the presence of a volcanic-plutonic arc complex in the Midland Valley during Ordovician times can adequately account for all of the above

points. Coarse conglomerates and associated sandstones would therefore represent the proximal fore-arc succession deposited in fault bounded basins possibly related to plutonic activity in the arc massif. The unroofing of successively younger high level plutonics intruded into a Moine-type basement on which the Ballantrae Complex was obducted can explain both clast composition and granite boulder ages. The Midland Valley arc would be flanked to the north by a marginal basin, represented by the Highland Border Complex (Bluck, 1984) and to the south by the proximal fore-arc sequence.

The recognition of the Southern Uplands as trench sediments has led to conflicting opinions about the location of an arc massif and position of any fore-arc basin during closure of the 'Iapetus Ocean'. Geophysical data show a > 6.4 km/s layer at 6 km depth below the Midland Valley. The interpretation that this layer represents a late Proterozoic basement comes mainly from granulite grade xenoliths taken from Carboniferous vents in the Midland Valley (Upton *et al.* 1983; Upton *et al.* 1984; Halliday *et al.* 1984). The 6.4 km/s layer extends northward into the Dalradian block with no apparent discontinuity across the Highland Boundary Fault but does show a change to considerably greater depths, c. 12 km, approximately 20 km north of the Highland Boundary Fault below the Dalradian block. From the geophysical evidence it is unclear as to the nature of the contact, though there is no evidence for the oceanic crust that would be consistent with a fore-arc basin beneath the Midland Valley.

The interpretation of the Ordovician sediments in Girvan as proximal fore-arc deposits (Bluck, 1983) which presently lie adjacent to trench sediments (the accretionary prism) suggests that the Southern Uplands Fault is not a simple reverse fault. Present day destructive margins have arc-trench gaps typically in excess of 60 km and rarely less than 150 km wide (Dickinson and Seely, 1979; Dickinson, 1973). If Bluck's interpretation is correct then the implication is that considerable crustal shortening has taken place along the northern margin of the Southern Uplands to close this gap or alternatively the missing fore-arc has been laterally displaced relative to the Midland Valley Ordovician magmatic arc.

Dewey and Shackleton (1984) have speculated that the 'Grenvillian' Midland Valley basement is similar to the Long Range Terrane in west Newfoundland and original continuity would suggest a 1000 km sinistral displacement along the Highland Boundary Fault. Most of the strike-slip motion is believed to have occurred before the end of the Llandovery as Upper Llandovery sediments deposited in the South Mayo Trough (Fig. 1.1), the Irish extension of the Highland Border Complex, overstep onto the Connemara metamorphic terrane believed to be Dalradian in age. However, the sedimentological similarities between the Highland Border Complex and the South Mayo Trough have been recently questioned by Williams (1987).

Hutton (1987) believes that sinistral slip occurred at two different times along the Clew Bay Fault, the westerly extension of the Highland Boundary Fault. The first movement took place in the Middle Ordovician as evidenced from the extensional cleavage and rotated porphyroblasts in the Dalradian metasediments and intrusives, 478 ± 12 Ma, of the Ox Mountains in southwest Ireland. The fault was inactive during the Llandovery and Wenlock but structural patterns similar to above affect Wenlock through Lower Devonian rocks on both sides of the Clew Bay Fault Zone. Magnetic evidence in Ireland indicates that the Dalradian block was thrust southwards over the Midland Valley block in Devonian and possibly Carboniferous times (Hutton, *ibid*). This may explain the change in depth of the 6.4 km/s layer approximately 20 km north of the Highland Boundary Fault.

The evidence that the Midland Valley had a separate history from the Dalradian block in the Ordovician and Silurian must lead to the conclusion that the simple relationship between the arc in the Grampian Highlands, fore-arc in the Midland Valley and trench sediments in the Southern Uplands needs considerable modification. The question arises as to whether the boundary between the Southern Uplands accretionary prism and the Midland Valley is analogous to the Highland Boundary Fault and is one which brings together two disparate blocks with different histories.

The 6.4 km/s pre-Caledonian basement layer is replaced by a 6.3 km/s layer at > 10 km south of the Southern Uplands Fault. Bamford (1979) suggests that this represents a fundamental break in the crystalline structure but does state the velocity variation, a difference of only 2%, could result from thermal and/or structural differences of one rock type. Leggett *et al.* (1983) has used the evidence from Halliday *et al.* (1979) on lack of inherited zircon U-Pb isotopic patterns in the Late Caledonian Granites to support Bamford's conclusion that the crust beneath the Southern Uplands and northern England is fundamentally different from the Midland Valley. Leggett (*ibid*) explains the lack of oceanic crust underneath both the Midland Valley and the Southern Uplands as subduction of thinned continental crust, originally part of the English northern margin (the Southern Uplands basement), underneath a continental buttress (the Midland Valley basement).

Hall *et al.* (1983,1984), Davidson *et al.* (1984) and Powell (1971) all cite geophysical evidence that the pre-Caledonian Midland Valley crust continues southward under the Southern Uplands. Granulite xenoliths recovered from Carboniferous vents in both the Northern Belt of the Southern Uplands (Upton *et al.* 1984) and southern parts of the Longford-Down inlier (Strogen, 1974), the Irish extension of the accretionary prism, supports the geophysical evidence that the Midland Valley crust is present under the Southern Uplands at least in the northern margin. This prompted Bluck (1983) to suggest that the

accretionary prism was thrust northward over the missing fore-arc onto the southern margin of the Midland Valley basement. Leggett *et al.* (1983) suggests that only a small portion of the Southern Uplands was involved in a northward thrust. Geophysical evidence indicates the present day expression of the Southern Uplands Fault is a northwestward directed thrust but earlier strike-slip translation across this boundary could have played a significant role in its evolution.

Leggett *et al.* (1983), Leggett *et al.* (1982), Barrett *et al.* (1982), McKerrow (1982) have evoked obduction of either an oceanic edifice or a slice of oceanic crust to explain the Ballantrae ophiolite. Accretion did not commence until after obduction of the Ballantrae Complex in Early Caradoc times, *c.* 480 Ma., (Mckerrow, 1986). Leggett *et al.* (1983) has suggested that if subduction was continuous during the intervening time strike-slip translation could explain the missing Llanvirn to Early Caradoc sediments in the accretionary wedge.

Repetition of quartz-poor and quartz-rich greywackes are characteristic of the Northern Belt greywackes in the Southern Uplands. Palaeocurrent data is variable with both dispersal from the margins and along the axis of the NE-SW trending basin. Although this data is equivocal a significant proportion of the NE-NW dispersed sediment are rich in andesitic detritus whereas the SE-SW dispersed sediments are compositionally more mature being rich in both quartz and metamorphics (Kelling *et al.* 1987). Walton (1963) initially suggested the presence of an ophiolitic landmass, 'Cockburnland', to explain the abundant southerly derived mafic detritus in the Ordovician flysch (tracts 1 and 3) sediments. More recently Kelling *et al.* (*ibid*) interpreted the diachronous introduction of volcanic detritus from the SW to the NE as the result of migration along a strike-slip fault of a tectonically displaced continental-arc oceanward of the accretionary prism.

Northwesterly derived Ordovician igneous-rich sandstones complicate the situation and led Mckerrow (1986) to invoke similarities with the northeastern North American coast where there is evidence that island-arc rocks collided with the Laurentian margin in Early Ordovician times. Mckerrow has proposed that northwesterly derived Ordovician arc-detritus and older continental crustal material, possibly Grenvillian in age, may have their ultimate source along the Laurentian North American margin. Sinistral displacement could have consequently moved both the accretionary prism and the arc north of the Southern Uplands northeastward.

A stratigraphic break coupled with a "distinctive fault fabric" that predates 400 Ma. minor intrusives and post dates accretion-related S1 cleavage led Anderson and Oliver (1986) to conclude that a 400 km sinistral slip occurred along the boundary between the Northern

belt and Central belt, namely the Orlock Bridge Fault in Ireland and Kingledores Fault in Scotland. The implication is that accretion of two similar but initially separate accretionary terranes took place along this boundary during the Silurian to early Old Red Sandstone times.

Arenaceous sediments give way to pelagic and hemipelagic fine-grained beds in the mid portion of the Southern Uplands, the 'Moffat Shale' basin. The arrival of coarse clastics in the basin, which was in existence from at least Caradoc times, was as late as Upper Llandovery (*turriculatus* Zone) in the central Southern Uplands with progressively earlier appearances away from the basin axis. Walton (1983) has pointed out the symmetrical filling of the basin, at least during Silurian times, is inconsistent with the accretionary prism model, essentially an asymmetrical basin. Murphy and Hutton (1986) follow this view and believe the Silurian succession in the Central and Southern Belts to be the deformed sediments of a filled symmetrical basin following arc cessation and thus unrelated to accretionary processes.

The Northern Belt has also been interpreted as back-arc basin sediments (Hutton and Murphy, 1987, Stone *et al.* 1987) and the 'Cockburnland arc', which supplied the northerly dispersed detritus to the Northern Belt, was subsequently displaced by strike-slip motion. Hutton (1987) indicates that the Midland Valley and Cockburnland arcs were initially one which has been repeated by sinistral slip along the Southern Uplands Fault. The authors however have failed to recognize that the Midland Valley arc has evidence of continental crust whereas the Cockburnland envisaged above is oceanic. Kelling *et al.* (1987) have also pointed out that the back-arc model does not account for the diachronous pattern of arc-detritus and continental blueschist detritus derived from the south.

Mineral ages of northwesterly derived detrital micas and southerly derived andesitic clasts in Caradoc age sediments in the Northern Belt have been determined by Kelley and Bluck (1989). The majority of detrital mica yields ages between 460 Ma. and 510 Ma. No micas as yet have yielded ages > 510 Ma. and older Grenville ages, which might be expected if the Southern Uplands lay south of the North American Laurentian continent. A metamorphic assemblage uplifted during the Ordovician was supplying detritus to the Northern Belt within 10 Ma. 465 Ma. hornblende bearing granites in the Southern Uplands Coarsewall Conglomerate contain schist xenoliths leading Kelley and Bluck (*ibid*) to suggest that a contemporary arc and its metamorphic basement may be the source for the southerly dispersed sediments in the Ordovician Southern Uplands. This in theory, could be the Midland Valley basement and Ordovician arc thus representing a major shortening along the Southern Uplands fault zone. As the fresh andesitic material yielded Lower to Middle Cambrian ages, 580 Ma. and 530 Ma, the source cannot be a contemporaneous Middle to Upper Ordovician island-arc as suggested by the back-arc basin model. The evidence is more

compatible with the displaced arc-terrane of Kelling *et al.* (1987).

Haughton (1988) has described clasts of flysch type sandstones from conglomerates in the Old Red Sandstone age Crawton Group, in the northeastern Midland Valley. Palaeoflow measurements show that the source lay to the south-southeast in the present day North Sea. Geochemically these sandstones suggest a possible mafic/ultramafic input derived from an ophiolitic complex of probable Ordovician age. Rb-Sr and Nd-Sm studies show that the Crawton Group sandstone clasts are isotopically distinct from the Southern Uplands sediments. The Midland Valley clasts and the Southern Uplands may have tapped two isotopically distinct source blocks on the Laurentian margin. However, significant isotopic variation is not seen between the Northern, Central, and Southern Belt sediments and implies that lateral accretion within the Southern Uplands may be less important than between the Southern Uplands and Midland Valley.

In summary, from the data we may conclude that during the Ordovician the Midland Valley was a site of a mature arc founded in continental crust of uncertain affinity. By Late Silurian-Early Devonian times a pile of greywacke with an input from mafic/ultramafic rocks supplied sediment to the eastern margin of the Midland Valley and may record the passage of strike-slipped blocks along the Laurentian margin (Haughton, *ibid*).

1.3 Purpose of the present investigation.

The evolution of the Midland Valley block in relation to the Southern Uplands block is still not well understood. The contact between the Southern Uplands and Midland Valley blocks may be analagous to the northern margin of the Midland Valley with two juxtaposed allochthonous 'terrane' each with separate Lower Palaeozoic histories. The present investigation of the Lower Old Red Sandstone conglomerates, specifically the Greywacke Conglomerate along the southern margin of the Midland Valley, will help define more closely the relationship between the Midland Valley block and Southern Uplands block during the Lower Palaeozoic times.

The Greywacke Conglomerate is exposed in a series of discontinuous outcrops just north of, and parallel to, the Southern Uplands Fault, (Fig. 1.2). The conglomerate has previously been regarded as forming the base of the Devonian (House *et al.* 1977). Although, fossil evidence is completely absent from the conglomerate Thirlwall (1988) has recently dated a major felsite intruded into the Greywacke Conglomerate at approximately 412 Ma. On the geological time-scale of Harland *et al.* (1982) this places the Greywacke Conglomerate in to at least Late Silurian times.

The purpose of the present investigation is to ascertain the interaction of the Southern Uplands block and the Midland Valley block during the Silurian-(?) Early Devonian time interval. In summary, the relationship between the Midland Valley and Southern Uplands has been interpreted in a number of ways but can be regarded as:

- 1). The Southern Uplands has always lain adjacent to the Midland Valley
- 2). The Southern Uplands is allochthonous, the contact with the Midland Valley being either a thrust or transform fault, or both.

In order to resolve the true nature of the contact between the two blocks and develop a better understanding of the history of their interaction a number of investigations have been undertaken. These focus mainly on the sedimentary history of the southern Midland Valley.

Recent advances in the knowledge of individual lithofacies and lithofacies associations in an alluvial system has led to a better understanding of the tectonic influence on sedimentation. With this in mind, a re-investigation of the sedimentation of the Greywacke Conglomerate is undertaken in Chapter 3. Using new palaeocurrent data and mindful of the ways in which directional structures are developed in fluvial systems, the dispersal of the Greywacke Conglomerate is re-appraised along with the lithofacies associations. In addition, the tectonic relationship of the source block to the basin of deposition will be re-evaluated.

Sandstone clasts taken from the Greywacke Conglomerate have been collected to represent as large an areal and vertical extent as possible. Petrographic analysis of each individual clast consist of either a ± 400 grain count or ± 100 granule count. In addition, a number of heavy minerals have been counted during the thin section point count. The results are given in Chapter 4 and are used for:

- (i) determining the composition and nature of the source block,
- (ii) comparing the sandstone clasts with published petrographic data from the Southern Uplands greywackes and,
- (iii) delineation of lateral trends associated with deposition of the Greywacke Conglomerate.

Geochemical analysis using X-ray Fluorescence for major and trace element chemistry are given in Chapter 5. The analyses provide an independent check on the reliability of the petrographic results. The intercorrelations between elements and their relationship to specific minerals are used to identify lateral and vertical compositional variation in the sandstones which may or may not have been obscured by post-depositional diagenesis. Major and trace element geochemistry is also used for comparison with published data available on

the Southern Uplands greywackes and similar clasts such as the northern Midland Valley Old Red Sandstone Crawton Group. Taken together the geochemistry and petrography will be used to characterize the source and define its tectonic setting.

In respect of the above investigations the Lower Palaeozoic geotectonic framework in the Southern Midland Valley is reviewed in Chapter 6. Here, the significance of the new data collected during the course of this research will be related to the present hypotheses concerning the Southern Uplands and Southern Midland Valley. A summary of the conclusions drawn from this thesis is given in Chapter 7.

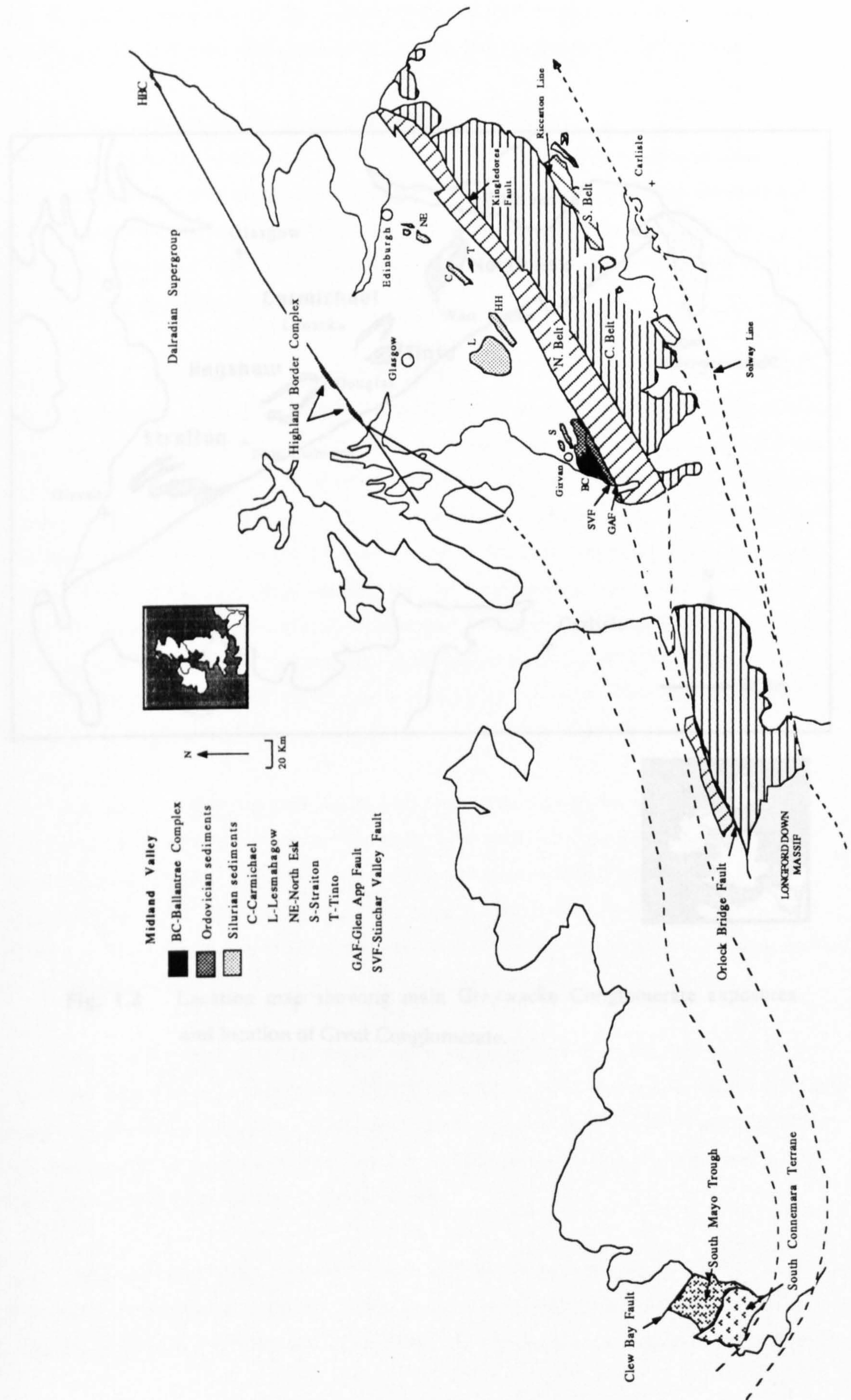


Fig. 1.1 Main Caledonian tectonic terranes in Scotland and Ireland

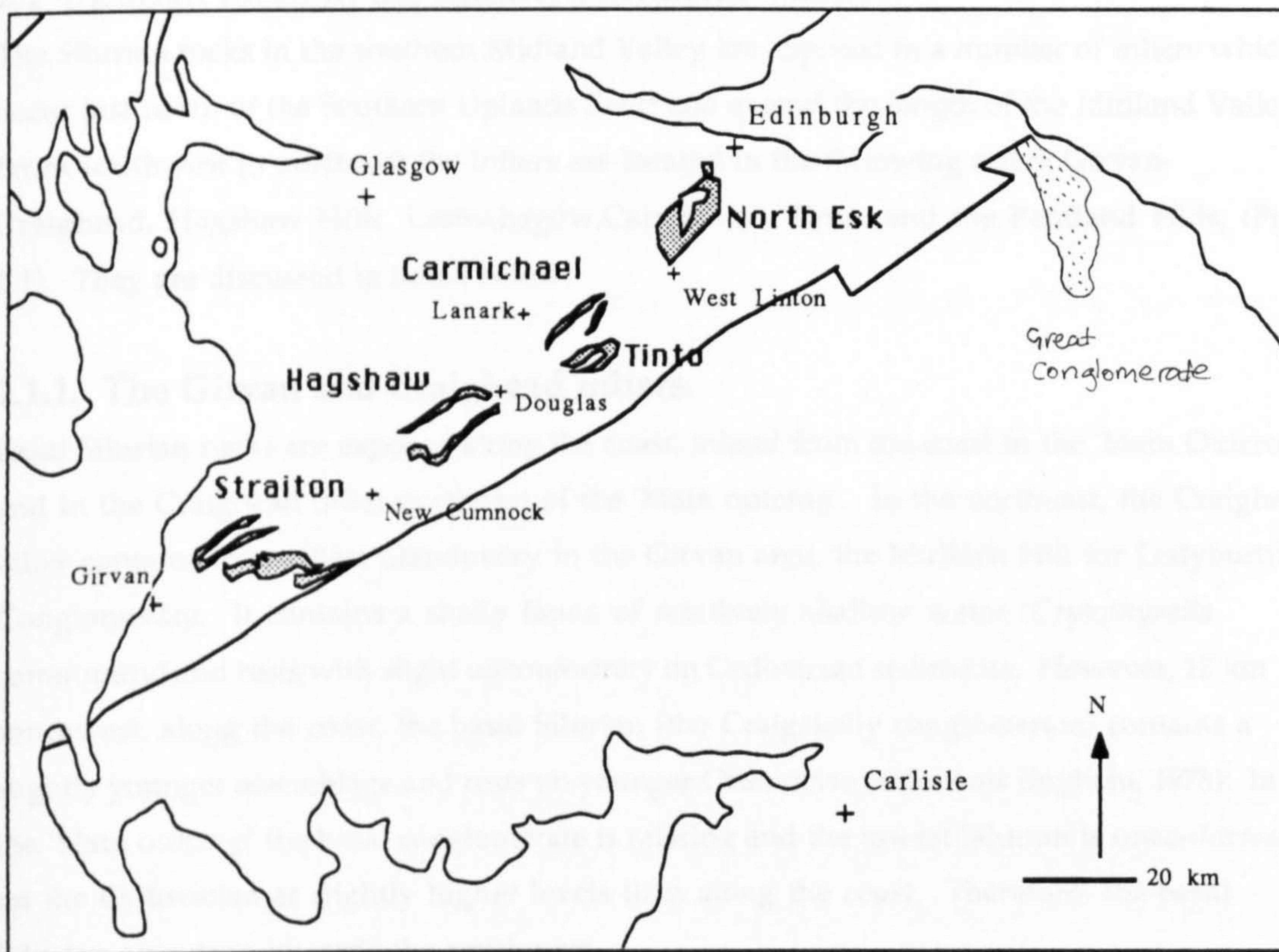


Fig. 1.2 Location map showing main Greywacke Conglomerate exposures and location of Great Conglomerate.

2.0 Regional geology of the Silurian-Devonian rocks in the southern Midland Valley and their relationship to the geotectonic framework

2.1 Silurian rocks in the southern Midland Valley.

The Silurian rocks in the southern Midland Valley are exposed in a number of inliers which occur just north of the Southern Uplands Fault and extend the length of the Midland Valley. From southwest to northeast the inliers are located in the following areas: Girvan-Craighead, Hagshaw Hills, Lesmahagow, Carmichael, Tinto, and the Pentland Hills, (Fig. 2.1). They are discussed in detail below:

2.1.1. The Girvan and Craighead inliers.

Basal Silurian rocks are exposed along the coast, inland from the coast in the 'Main Outcrop' and in the Craighead inlier northeast of the 'Main outcrop'. In the northeast, the Craighead inlier contains the earliest Llandovery in the Girvan area, the Mulloch Hill (or Ladyburn) Conglomerate. It contains a shelly fauna of relatively shallow water (*Cryothyrella* community) and rests with slight unconformity on Ordovician sediments. However, 12 km southwest, along the coast, the basal Silurian (the Craigs Kelly conglomerate) contains a slightly younger assemblage and rests on younger Ordovician sediments (Ingham, 1978). In the 'Main outcrop' the basal conglomerate is missing and the lowest Silurian is unconformable on the Ordovician at slightly higher levels than along the coast. Therefore, the basal Silurian oversteps towards the southwest.

A series of sandstones, grits, shales, and mudstones occupy the majority of the Llandovery succession near Girvan. The majority of the sandstones and grits show typical turbiditic associations (Cocks and Toghil, 1973) and the mudstones and shales contain graptolitic horizons. The graptolite zones compare closely with the Gala Group, Hawick Rocks and Riccarton Group of the Moffat area in the Southern Uplands Southern and Central Belts indicating the 'Iapetus Ocean' basin was sufficiently closed by the Llandovery.

Cocks and Toghil (*ibid*) have taken the Knockgardner Fm. as the base of the Wenlock. This formation contains a suite of brackish or fresh water fossils distinct from the marine faunas in the Llandovery sediments. The Knockgardner Fm. is overlain by 'red beds' (the Straiton Grits) the development of these continental facies was probably later in the Girvan area than in the inliers to the northeast.

The Llandovery conglomerates in the coastal section have been studied by Bluck (1983). The basal conglomerates on the coast, the Craigs Kelly conglomerate, contain clasts of acidic volcanic, porphyritic, granitic, and subordinate basic fragments, vein quartz, and quartzites,

clearly reflecting an overall trend from a basic source in the Ordovician to an increasingly acidic source in the Silurian (Bluck, *ibid*). However, granitic debris diminishes in importance giving way to fine-grained acidic volcanics. Upward through the section there is an increase in vein quartz and metamorphic quartzites at the expense of basic and porphyritic constituents but in the Scart Grits, at the top of the section, a reduction in the quartz rich fragments at the expense of increased basic fragments occurs.

Palaeoflow data from the conglomerates show a dispersal from the N or NW. Bluck (1983) suggests that a basement mainly composed of metamorphic, granitic and acid volcanics was uplifted N-NW of Girvan and filled a narrow fault bounded basin probably accounting for the southwesterly overstep and northerly source.

2.1.2. Hagshaw Hills inlier.

The lowermost exposed Silurian in the Hagshaw Hills is represented by the Hagshaw Group. The basal units of the Hagshaw Group are interpreted to be marine turbidite sediments derived from the south and have been dated as Upper Llandovery (Rolfe, 1961). The Hagshaw Group is overlain by the Parisholm Conglomerate (Igneous Conglomerate). The presence of Wenlock age fossils found in the conglomerate has led Rolfe and Fritz (1966) to suggest a disconformity at the base of the conglomerate. The Parisholm Conglomerate was studied by McGiven (1967), who concluded from sedimentological evidence that the conglomerate was deposited in a subaerial alluvial fan environment supporting the presence of a disconformity.

The Parisholm Conglomerate is succeeded by the Glenbuck Group. The latter is interpreted as an alternating sequence of marginal marine and terrestrial redbeds (McGiven, 1967; Rolfe, 1961), there being a distinctive fish-bed horizon within this group. Although, the fish-beds contain a rich fauna an accurate palaeoenvironmental interpretation can not be made, though assumed by Rolfe to be deposited in a lacustrine or lagoonal environment.

The Glenbuck Group is overlain by the Hareshaw conglomerate (Quartzite Conglomerate). This conglomerate is again best explained as a terrestrial alluvial fan deposit (McGiven, 1967, Walton, 1983).

The Quarry Arenite lies between the Hareshaw Conglomerate and the Lower Old Red Sandstone. The sediments are medium to coarse-grained arenites and subgreywackes and are best explained as channel and floodplain deposits in a braided stream environment (McGiven, 1967).

2.1.3 The Lesmahagow Inlier.

The Lesmahagow inlier is located approximately 8 km to the north of the Hagshaw Hills inlier. The Priesthill Group forms the base of the exposed Silurian. Turbidite features are common in the Partick Burn Fm., the lowest most formation of the Group. The upper formations in the Group consists of marine sandstones, shales and mudstones lacking sedimentological evidence for a turbidite origin (McGiven, 1967).

The Priesthill Group is conformably overlain by the Waterhead Group, a series of medium to fine-grained sandstones, silty mudstones and mudstones. The Igneous Conglomerate is absent from the succession but the base of the Waterhead Group shows signs of being transitional from marine to terrestrial (McGiven, *ibid*).

The Middlefield Conglomerate (Quartzite Conglomerate) forms the basal member of the overlying Dungavel Group. A series of fluvial medium-grained sandstones, the Plewlands Formation, passes conformably into the Lower Old Red Sandstone

2.1.4. The Tinto and Carmichael inliers.

The Tinto and Carmichael inliers lie approximately 12 km to the NE of the Lesmahagow and Hagshaw Hills inliers. Silurian rocks are very poorly exposed in both these inliers.

In the Tinto region greywackes and shales pass upward into mudstones and shales of similar lithology to the upper fish-beds of the Lesmahagow inlier (Peach and Horne, 1899). The Quartzite Conglomerate is well developed but poorly exposed and Read (1927) noticed it passed westward into sandstones with thin conglomeratic horizons, in turn overlain by variegated flaggy sandstones.

The Silurian rocks in the Carmichael area are better exposed than in the Tinto district and have been described by Rolfe (1960). The oldest exposed rocks are the Carmichael Burn Group, the majority of which are mudstones. The Carmichael Burn Group is overlain by the Fence Conglomerate (Igneous Conglomerate) where the latter is more typical of a pebble conglomerate. Very poorly exposed sandstones occur between the Fence Conglomerate and the Kirk Hill Conglomerate (Quartzite Conglomerate). The Quartzite Conglomerate does not have continuous exposure, although Rolfe (*ibid*) noticed the conglomerate thins towards the southwest. The Quartzite Conglomerate is overlain by a coarse subgreywacke with pebbles of quartz and chert. The contact between these sandstones and the Lower Old Red Sandstone is not exposed.

2.1.5 The Pentland Hills inlier.

In the Pentland Hills, the Silurian is exposed in three inliers separated by outcrops of the Lower and Upper Old Red Sandstones. Of the three inliers the North Esk contains the most complete section of Silurian rocks in the Pentlands district.

The basal North Esk Group comprises, in ascending order, the Reservoir, Deerhope, Wether Law Lin, and Henshaw Formations. The Reservoir Formation is a 300 m sequence of mudstones, siltstones, and fine-grained flaggy grits. A 25 cm thick limestone (the Rottenstone) with a varied shelly fauna, including crinoid columns and a number of corals, is found near the middle of the Reservoir Fm. Eurypterid-bearing micaceous grits associated with the limestones are transitional into more argillaceous units which have yielded a number of starfish. Cross-bedding in the grits and siltstones suggests the source lay to the east-northeast (Mykura and Smith, 1962).

The Deerhope Fm. is characterized by basal flaggy sandstones overlain by 35 m of pebbly conglomerates and conglomeratic sandstones which in turn are followed by micaceous sandstones. The conglomeratic unit, the Haggis Grit, contains pebbles of quartzites, cherts, porphyries, microgranites, altered sub-basic lavas and indurated sediments up to 2 cm in diameter (Mykura and Smith, *ibid*). Tipper (1976) records marked lateral changes from NE-SW within this formation. The conglomerates pinch out towards the SW and the overall trend in the lower sandstones is towards a finer grained size in that direction, consistent with the data from the Reservoir Fm. Marine faunas have been recorded from the micaceous sandstones and a sharp decrease in fossil abundance is accompanied by a decrease in mica, defining the upper boundary of this formation.

The Wether Law Lin Formation contains a series of fossiliferous mudstones and siltstones. Five bio-stratigraphic units are recognized by Tipper (*ibid*):

Unit a: fauna include deeper water brachiopods dominated by *Skendioides* and *Dicoelosia*.

Unit b: volcanic ash.

Unit c: brachiopod fauna is dominated by *Eoplectodonta* and *Vibyella* whereas *Skendioides* and *Dicoelosia* are almost totally absent. Within this unit two thin ash bands occur.

Unit d: occurrence of shallower-water brachiopods *Entomis*, *Pentandella*, and *Platyschisma*.

Unit e: characterized by shallower-water brachiopods *Entomis*, *Pentandella*, and *Platyschisma*.

In conclusion, the fauna suggest a change from a deeper-water environment upwards into

shallower-water.

This regressive sequence is succeeded by red sandstones and the Igneous Conglomerate which form the base of the Henshaw Formation. The Igneous Conglomerate contains boulders up to 30 cm in diameter (Mykura and Smith, 1962). Red sandstones separate the Igneous Conglomerate from the Quartzite Conglomerate, the latter being only 2 m thick and thinning toward the southwest. The Quartzite Conglomerate is followed by a series of argillaceous beds and sandstones. The lower mudstones have yielded fish fragments and are overlain by red sandstones with lenses of pebbly grits containing vein quartz, acid-lavas and mudstones. Current directions suggest the source for the mudstones and sandstones is to the east (Mykura and Smith, *ibid*). The sandstones are succeeded by another sequence of mudstones, siltstones, and sandstones which have yielded fish fragments, a sponge, and crinoid stems suggesting a marine environment. The uppermost Silurian comprises sandstones which rest with a slight unconformity on the preceding mudstones and pass upwards into the Lower Old Red Sandstone.

2.1.6. Discussion of the Midland Valley Silurian sediments and their relationship to the Southern Uplands.

Marine conditions continued from the Ordovician into the Silurian where the Llandovery throughout the Midland Valley, is represented by predominately deep water turbidites. Palaeocurrent data suggest that, in at least the Hagshaw Hills and the Lesmahagow inlier (see above and Leggett, 1980), these sediments were derived from the south. This led McKerrow, *et al.* (1977) to reinterpret the 'Cockburnland' land mass, originally proposed as a source for the abundant southerly derived mafic detritus in the Ordovician Southern Uplands (Walton, 1963, Walton and Weir, 1977) as a Southern Uplands accretionary prism emergent trench-slope break uplifted in Llandovery times which shed detritus into the Midland Valley. In this model, the Midland Valley in Llandovery times is an upper slope fore-arc basin with a presumed sediment source from the south. However, the equivalent formations in the North Esk inlier show sediment dispersal from the east-northeast. Also, in the Girvan inliers local structural basins were active in the earliest Llandovery where acidic and metamorphic basement material continued to be derived from the northwest.

A regression is seen in all the inliers during the latest Llandovery or earliest Wenlock and culminated in the deposition of the Igneous Conglomerate interpreted as terrestrial alluvial fan sediments (McGiven, 1967). McGiven showed that the Igneous Conglomerate is very similar in all the inliers and concludes that the formation may represent a time equivalent unit. The Igneous Conglomerate is, however, missing in the Lesmahagow area, where marine turbidites pass into reddened beds with mudcracks also indicating a terrestrial origin.

McGiven suggested the Igneous Conglomerate was sourced from the southwest and overlying sandstones show a dispersal towards north-northwest. However, the Igneous Conglomerate is more a pebble conglomerate in Hagshaw Hills, Tinto and Carmichael inliers and completely absent in the Lesmahagow inlier with the coarsest material recorded in the North Esk suggesting a source to the NE. McGiven suggests that the constituents in the conglomerates resemble material presently exposed in the Southern Uplands and the present day Southern Uplands Fault or its predecessor formed the southern margin of the basin which sourced the Silurian sediments in the Midland Valley.

Six main lithological groups are recognized in the clasts within the Igneous Conglomerate: i). fine-grained igneous clasts composed mainly acidic in composition but also include basaltic and andesitic volcanics (74%), ii). coarse-grained granitic clasts and rare medium-grained intermediate clasts (6%), iii). sedimentary 'greywacke' clasts (6%), iv). metaquartzites and rare schists (3%), v). chert and cherty mudstone (10%) and, vi). vein quartz (0.3%). Although coarse conglomerates with similar composition occur in the Southern Uplands, it is difficult to reconcile the widespread nature and abundance of igneous material in the Igneous Conglomerate with derivation from an essentially sedimentary Southern Uplands.

The Igneous Conglomerate was not deposited in the Lesmahagow inlier only 8 km to the north of the Hagshaw Hills and the postulated equivalent formations are either marginal marine or terrestrial floodplain deposits. Variation on such a small scale could possibly imply that sedimentation during the Upper Llandovery-Lower Wenlock was subject to more by localized structural control than by a major faultscarp to the southeast or more simply the Lesmahagow sediments represent distal-fan sediments along an east-west trending fan-surface. A filling of the Midland Valley from easterly sourced sediments could also explain the introduction of terrestrial sediments at latter times in the Girvan inliers.

The sediments between the Igneous and Quartzite conglomerates are distal braided stream, floodplain and lacustrine or marginal marine deposits and record the progressive denudation of the source area before renewed activity in the source gave rise to the Quartzite Conglomerate. The Quartzite Conglomerate although coarser than the Igneous Conglomerate has properties (lithological, compositional) which indicate it is a discrete lateral time equivalent. Again, McGiven (*ibid*) has suggested derivation from the southeast for both the sandstones and the Quartzite Conglomerate.

The conglomerate contains the same clast constituents as the Igneous Conglomerate but in different proportions, both metamorphic (15%), and vein quartz (31%) have increased at

the expense of fine-grained igneous fragments (32%). There is no significant change in sedimentary (9%) and chert (7%) clasts, though coarse-grained igneous clasts are extremely rare. In the Girvan inliers dilution of igneous material by vein quartz and metaquartzites occurs earlier in the Lower Llandoverly.

Northwest and southeast dispersal of acid-volcanics and granitic material into the Silurian basins in the Midland Valley led Bluck (1983) to suggest the Midland Valley was an interarc-basin flanked by mature arc volcanics and plutonics. Again, it is difficult to reconcile derivation of the conglomerates from the Southern Uplands and Bluck (1983; 1985) proposed an extension of the Midland Valley Block beneath the thrustured Southern Uplands as the source for the Silurian conglomerates. As noted earlier, the Quartzite Conglomerate in the Tinto, Carmichael and North Esk inliers thins to the southwest and is in contrast to derivation from the southeast.

With gradual erosion of the source area braided streams flowing predominately to the north-northwest at approximately 350° replace the more proximal conglomerates (McGiven, 1967). The exception is the North Esk inlier which shows a finer-grained assemblage of terrestrial floodplain deposits overlying a very thin development of the Quartzite Conglomerate and containing a marine transgressive unit. Mykura and Smith (1962) indicate that directional currents in the sandstones above the Quartzite Conglomerate in the North Esk inlier suggest a source to the east.

2.2. Lower Old Red Sandstone rocks in the southern Midland Valley.

The Highland Boundary Fault and Southern Uplands Fault control the present day outcrop of the Lower Old Red Sandstone which is almost wholly confined to the Midland Valley in Scotland. In the Midland Valley, the Lower Old Red Sandstone is unconformably overlain by the Upper Old Red Sandstone, representing a major unconformity during Middle Old Red Sandstone times. The Old Red Sandstone throughout the Midland Valley is obscured by Carboniferous cover.

The Lower Old Red Sandstone in the Midland Valley consist of a series of 'red beds' ,fluvial sandstones and conglomerates, and subaerial lavas. The sediments were deposited in two elongate 'troughs; the 'Strathmore basin' in the north and the 'Lanark basin' in the south (Bluck, 1978). These basins parallel the Caledonian trend where the regional palaeoslope was towards the southwest.

The Lower Old Red Sandstone in the southern Midland Valley, the Lanark basin, reaches an estimated thickness of up to 2000 m in the northeast (Mitchell and Mykura, 1962)

thinning to 1500 m in the far southwest (Bluck, *ibid*). The sediments are not exposed in a continuous fashion but instead occur in isolated patches just north and along the length of the Southern Uplands Fault, the best exposures being associated with the Silurian inliers. Lack of continuity and almost virtual absence of fossils has prohibited a detailed correlation and lithostratigraphic analysis.

The Lower Old Red Sandstone in the Southern Midland Valley comprises the basal Greywacke Conglomerate, overlain by a thick sequence of lavas interstratified with fluvial sandstones near the base, the Lava Conglomerate, and finally another sequence of fluvial sandstones.

2.2.1. The Greywacke Conglomerate.

The basal Greywacke Conglomerate has been previously studied by McGiven (1967) who looked at exposures in the Hagshaw Hills, Carmichael, Tinto, and Pentland Hills. This section outlines the interpretations and conclusions formed by McGiven. The Greywacke Conglomerate forms the basis for the present investigation and previous work will be integrated and reinterpreted following the conclusions made in this study.

Conclusions and Summary from McGiven (1967):

- 1). The conglomerate can be divided into two main facies defined as type 1 and type 2.

Type 1 facies is characterized by poorly-sorted, thick (1 m) conglomerates with or without a 20 cm (6") medium-grained sandstone occurring near the top of the bed. Bedding is poorly defined, channelling is absent but small-scale erosion into underlying conglomerate beds is common. Where bedding is discernable it is laterally continuous. Directional structures are absent. Type 1 facies has been interpreted as sheetflood (debris flow) sediments deposited on alluvial fans.

Type 2 facies is confined to the upper 3-15 m of conglomerate and characterized by slightly better sorted, finer-grained conglomerates, a few cms to 4 m thick again topped by a thin sandstone. Sandstone forms a significantly larger portion of the association with the finer-grained conglomerate which can be seen to channel into the underlying sands. Cross-bedding in the sandstones give a mean palaeoflow directed towards the northwest at 345°. However, current lineation show sediment dispersal was toward 315°. Type 2 facies have been interpreted as a streamflood sediments deposited on alluvial fans.

- 2). Positive correlation exists between maximum clast size and individual conglomerate bed thickness in both Type1 and Type 2 facies.

- 3). There is no systematic vertical change in maximum clast size except in the very top few metres suggesting that uplift in the source kept pace with erosion.
- 4). Maximum clast size and formation thickness increase to the southeast, similar to both the Igneous and Quartzite Conglomerates.
- 5). The overall composition of the Greywacke Conglomerate is similar to the Silurian conglomerates but sedimentary clasts (greywackes) form up to 84% in the 16-32 mm range. The exception is the conglomerate located near Carmichael where the composition more closely resembles the Quartzite Conglomerate.
- 6). Compositional maturity measured as quartzite + vein quartz + chert over all other clast types is lowest in the Greywacke Conglomerate when compared with the Igneous and Quartzite Conglomerates.
- 7). Clasts from the Greywacke Conglomerate can be readily matched with known lithologies in the Southern Uplands. Chert, and fine-grained igneous fragments resemble the Ordovician. However, greywacke clasts are more acidic than the Ordovician and more closely resemble the Silurian sediments.
- 8). Roundness calculations show that quartzite and vein quartz have higher roundness values than would be expected for first cycle deposits. It was concluded that the two clast compositions are at least second cycle and probably derived from older conglomerates with similar clasts located in the Southern Uplands.
- 9). Measurements of maximum clast size, roundness, shape, and composition all confirm the source direction was to the southeast. These measurements also suggest that in the Hagshaw Hills a separate source lay to the west. It was envisaged that at least two separate fans were active in this area.

The sediment dispersal and proximal nature of the Greywacke Conglomerate along with the abundance of sedimentary clasts resembling the Southern Uplands led McGiven to the conclusion that the Greywacke Conglomerate was derived from the present day Southern Uplands. The present day Southern Upland Fault or its ancestor was active during Old Red Sandstone times and formed the basin margin from which alluvial fans were dispersed toward the north-northwest.

The Northern Belt sediments are at present in fault contact with the Midland Valley and renewed activity along this fault should have shed abundant mafic-rich greywackes into

the Midland Valley basin. McGiven himself noted the siliceous nature of the greywacke clasts and indicated the clasts more closely resemble the Silurian Southern Uplands. This led Bluck (1983) to suggest the Greywacke Conglomerate may record the emplacement of the "allochthonous Silurian Southern Uplands" over the Midland Valley. In this model, the present Southern Uplands Fault could not have played a significant role during deposition of the Greywacke Conglomerate. It is however difficult to imagine the entire accretionary prism thrust northwards over a supposed fore-arc with only the Silurian succession forming the highlands.

George (1960) also questioned the control of the Southern Uplands Fault on the sedimentation in the Midland Valley during Old Red Sandstone times. Lower Old Red Sandstone outliers south of the fault and the abrupt truncation of the conglomerate by the fault were cited as evidence for post Lower Old Red Sandstone movement along the Southern Uplands Fault.

Recent evidence has also shown that a thick assemblage of conglomerates, the Great Conglomerate, exposed in a narrow N-S fault bounded basin in the eastern Southern Uplands and previously regarded as Upper Old Red Sandstone in age, are now thought to be Lower Old Red Sandstone in age (Davies *et al.* 1986; Rock and Rundle, 1986). The Great Conglomerate unconformably overlies the Silurian greywackes and indicates the Southern Uplands was receiving, rather than supplying, detritus during the Lower Old Red Sandstone times. The Great Conglomerate is very similar to the Greywacke Conglomerate with abundant sandstone clasts and may be its equivalent. The palaeoflow in the Great Conglomerate is directly to the west.

The Greywacke Conglomerate in the Tinto, Carmichael and North Esk regions is cut by a series of felsite intrusions. The Tinto Felsite has been dated at 414.9 ± 1.9 Ma. (Thirlwall *et al.* 1986) revised to 411.9 ± 1.9 Ma (Thirlwall, 1988). The age of the Silurian-Devonian boundary is uncertain but recent isotopic evidence suggests the boundary is close to 412 (Thirlwall, 1988). This clearly places the age of the Greywacke Conglomerate in the latest Silurian, possibly spanning the Silurian-Devonian boundary.

The Greywacke Conglomerate passes upward into a sequence of red and grey lithic arenites, containing occasional small-scale trough and planar cross strata. These sandstones have a dispersal towards the southwest. The sandstones were not studied in detail, but have features suggesting a shallow braided stream origin.

2.2.2. Old Red Sandstone Lavas.

A thick pile of mixed andesitic, basaltic, trachytic, and rhyolitic lavas are interstratified with lithic-arenites. These units, in general, overlie the conglomeratic-sandstone package of the Greywacke Conglomerate and associated sandstones.

In the Pentland Hills, 2000 m of lavas thin towards the southwest by pronounced overlap in this direction of the upper lavas onto the fluvial sediments (Mitchell and Mykura, 1962). In the Carmichael, Tinto, and Hagshaw Hills region faulting in the area obscures the boundary between the lavas and the fluvial sandstones overlying the Greywacke Conglomerate. Toward the southwest, in the Straiton area, the lavas are interstratified with the upper parts of the fluvial sandstones which contain conglomeratic bands similar to the Greywacke Conglomerate.

According to Thirlwall (1981) the lavas are calc-alkaline consistent with subduction above the northwestern margin of the Iapetus Ocean. Since the closure of the Iapetus was thought to be complete by Devonian times this led Thirlwall to suggest that the Old Red Sandstone Lavas are Silurian in age thus predating final closure of Iapetus. Thirlwall (1988) has recently indicated an age of 412.6 ± 5.7 Ma for the lavas in the southern Midland Valley consistent with the age for the Tinto felsite. This places the age of the magmatism very close to Silurian-Devonian boundary. If this evidence is accepted then more importantly, from the point of view of this thesis, it indicates that the Greywacke Conglomerate was deposited prior to the final closure of the Iapetus Ocean and could not be a continental molasse associated with continent-continent collision.

A sequence of Lower Old Red Sandstone lavas occurs just south of the Southern Uplands Fault along the Berwickshire Coast at St. Abbs Head which are chemically similar to the Midland Valley lavas. To preserve the arc-trench gap seen in modern analogues Thirlwall (*ibid*) suggested a two stage emplacement of the Southern Uplands. The first record of emplacement is recorded by the Greywacke Conglomerate which brought the northern half of the Southern Uplands in contact with the Midland Valley. The southern half still lay far to the south thus preserving the arc-trench gap and only later was brought into contact with the accreted Midland Valley margin. In this model the clasts from the Greywacke Conglomerate would be lithologically identical to the Ordovician sediments in the Southern Uplands. It has already been stated that there are problems in matching the clasts from the Greywacke Conglomerate to the adjacent Northern Belt sediments in the Southern Uplands and this point is again addressed in Chapter 6.

2.2.3. The Lava Conglomerate and associated sandstones.

The upper parts of the lavas are interstratified and pass into another sequence of sandstones and conglomerates. The conglomerates consist entirely of clasts whose compositions closely resemble the underlying lavas. A reconnaissance study of the Lava Conglomerate gave the following results.

In the Lava Conglomerate two separate facies have been recognized by the author; a coarse conglomerate facies and a pebbly sandstone facies:

1). The conglomerate facies is a very coarse-grained conglomerate with a mean maximum clast size (average of the ten coarsest clasts in 1 sq metre) up to 37.1 cm. Bedding is very poorly defined and the conglomerate as a whole resembles the Greywacke conglomerate as a poorly sorted, well rounded coarse sediment. Imbrication is not a common feature and is probably a function of the high degree of rounding of the clasts. The matrix is a very coarse sandstone to granule grade.

2). Pebble conglomerates and pebbly sandstones are much more common in these conglomerates when compared with the Greywacke Conglomerate. The pebble conglomerates and sandstones are commonly associated with beds of coarser poorly-sorted conglomerates. Within this association, erosional features are absent and the coarser conglomerates do not have channelled lower surfaces. The finer conglomerates and pebbly sandstones show abundant small to medium scale trough cross-stratification and grade laterally and vertically into finer cross-bedded sandstones. In some areas, the pebbly sandstone is overlain by thin mudstones exhibiting dessication cracks.

The coarse conglomerate facies texturally resemble the Greywacke Conglomerate and were probably deposited by sheetfloods in a proximal alluvial-fan environment. In the pebble conglomerate-sandstone association, distal braided stream deposits would be the most likely depositional environment.

The clast lithologies are all volcanic with a dominance of andesite, amygdaloidal or vesicular basalt and rhyolite. Lithologies which are present in the Silurian conglomerates are completely absent in these conglomerates. The composition of the clasts in any particular area can be readily matched with nearby outcrops of the underlying lavas.

Figures 2.2.1 and 2.2.2 shows dispersal vectors taken from cross-strata (pebble conglomerate association) and rare imbricated clasts (coarse conglomerates) and mean maximum clast size taken from coarse conglomerates. Palaeoflow vectors indicate that at least some of the conglomerates were derived from the south but the best exposures, where

reliable palaeoflow data have been obtained, indicate a derivation from the north-northeast, north-northwest and east, *i. e.* from within the Midland Valley. Maximum clast size variation shows a consistently coarse grain size close to the Southern Uplands Fault but coarse conglomerates occur along the northern limit of the exposures as well.

There are a few points which can be made with reference to the Lava Conglomerate:

- 1). The source for the clasts appears to be underlying or possibly contemporaneous lavas.
- 2). A source for the clasts in the region of the Southern Uplands is possible, but lavas now exposed north of the Southern Uplands are equally likely to be the source
- 3). There is no reason to infer a cover of lava over the Southern Uplands as suggested by Bluck (1983).

2.2.4. The Structure of the Lower Old Red Sandstone.

The regional structure of the Silurian-Devonian is a series of broad folds plunging towards the northeast. The fold structure is best seen in the Hagshaw Hills area where it affected both the Silurian and conformably overlying Lower Old Red Sandstone. In the Hagshaw Hills inlier the main structure is an overturned asymmetrical anticline. The fold axis is cut by two reverse faults which bring the oldest Silurian to the surface (see Fig. 3.2.3). The rocks in the southern limb of the fold are steeply dipping or overturned whereas the rocks in the northern limb have an average dip between 30°-40°. In the northern limb a series of N-S trending faults have been mapped and a number of these faults terminate against the northern-most thrust in the core of the anticline.

The basal Lower Old Red Sandstone shows a stepped appearance at progressively higher levels to the northwest. In the far northeastern exposures the Greywacke Conglomerate has been mapped on the presence of greywacke clasts found in peat runnels. Slightly further southwest the basal Greywacke Conglomerate is a sandstone, a coarse conglomerate being absent. Rolfe (1961) has pointed out that a plane of unconformity may well account for the outcrop pattern, poor exposure in the northern limb preventing either hypothesis (faulting or unconformity) to be proven.

The NE-SW trending faults in the core of the anticline are no doubt associated with the folding and are thought to be Caledonian in age. The N-S trending faults both cut the earlier Caledonian faulting in two places and parallel the Hercynian trend, and is therefore thought to be Hercynian in age.

In the Carmichael inlier the structure is again an anticline but only rocks in the northern limb are exposed. The beds dip at approximately 20°-35° toward the northwest. The Carmichael Fault, another NE-SW trending structure, separates the Carmichael inlier

from the Tinto to the south. In the Tinto region the Silurian and Lower Old Red Sandstone rocks dip at approximately 40° to the north.

In the Pentland Hills the basal Greywacke Conglomerate lies unconformably on the near vertical Silurian which strike at N 30° E. In the Straiton area the basal Old Red Sandstone unconformably overlies both the Ordovician and Silurian strata, which show dips up to 45°. The implication is that the basal Old Red Sandstone was deposited on a deformed and eroded pre-ORS surface along the flanks of the Southern Midland Valley. In the mid-region of the Midland Valley sedimentation was continuous and the onset of deformation was later. In the Straiton area a number of NE-SW trending faults cut both the underlying Ordovician-Silurian and the Old Red sediments, though some faulting can be proved to be of pre-Old Red Sandstone in age.

2.3. Summary of previous views on the Silurian-Devonian rocks in the southern Midland Valley.

The Southern Uplands sedimentary sequence has been interpreted as representing the accretionary wedge formed along the northern margin of the north dipping subduction zone during closure of the Iapetus Ocean (Mitchell and McKerrow, 1975; Leggett, 1980). It has been suggested that emergence of the trench-slope break in the Southern Uplands accretionary prism during Silurian times formed a continuous ridge (McKerrow *et al.* 1977) which was the source for the Late Silurian marine sandstones in the Midland Valley (Leggett, 1980). Continual uplift of both the Southern Uplands accretionary prism and the adjacent Midland Valley fore-arc culminated in the deposition of molasse type conglomerates and sandstones in the Midland Valley, (Leeder, 1982). Complete closure of the 'Iapetus Ocean' is regarded to have taken place by Mid Devonian times, the culmination resulting in the folding of the Siluro-Devonian sediments into a series of broad anticlines and synclines.

Bluck (1983) gives a convincing argument for re-evaluating the Silurian rocks in the Southern Midland Valley and suggests the sediment source may not be in the present day Southern Uplands. The Midland Valley is thought to be an arc-inter-arc basin flanked by mature arc volcanics and plutonics during the Lower Palaeozoic. The Greywacke Conglomerate may thus record the emplacement of the Southern Uplands over the Midland Valley on a large thrust.

The regressive nature of the basin infill is consistent with both the Midland Valley inter-arc model and the gradual emergence of the Midland Valley fore-arc model. However, both the models are dependent on dispersal of the sediments from the south-southeast but the equivocal nature of palaeocurrent data cast doubt on the conclusions. The contact between these two blocks may be analagous to the northern margin of the Midland Valley with two

laterally juxtaposed 'terrane' with separate histories during the Lower Palaeozoic. Thus, the relative position of the two terranes today may not necessarily have been the same during the Lower Palaeozoic.

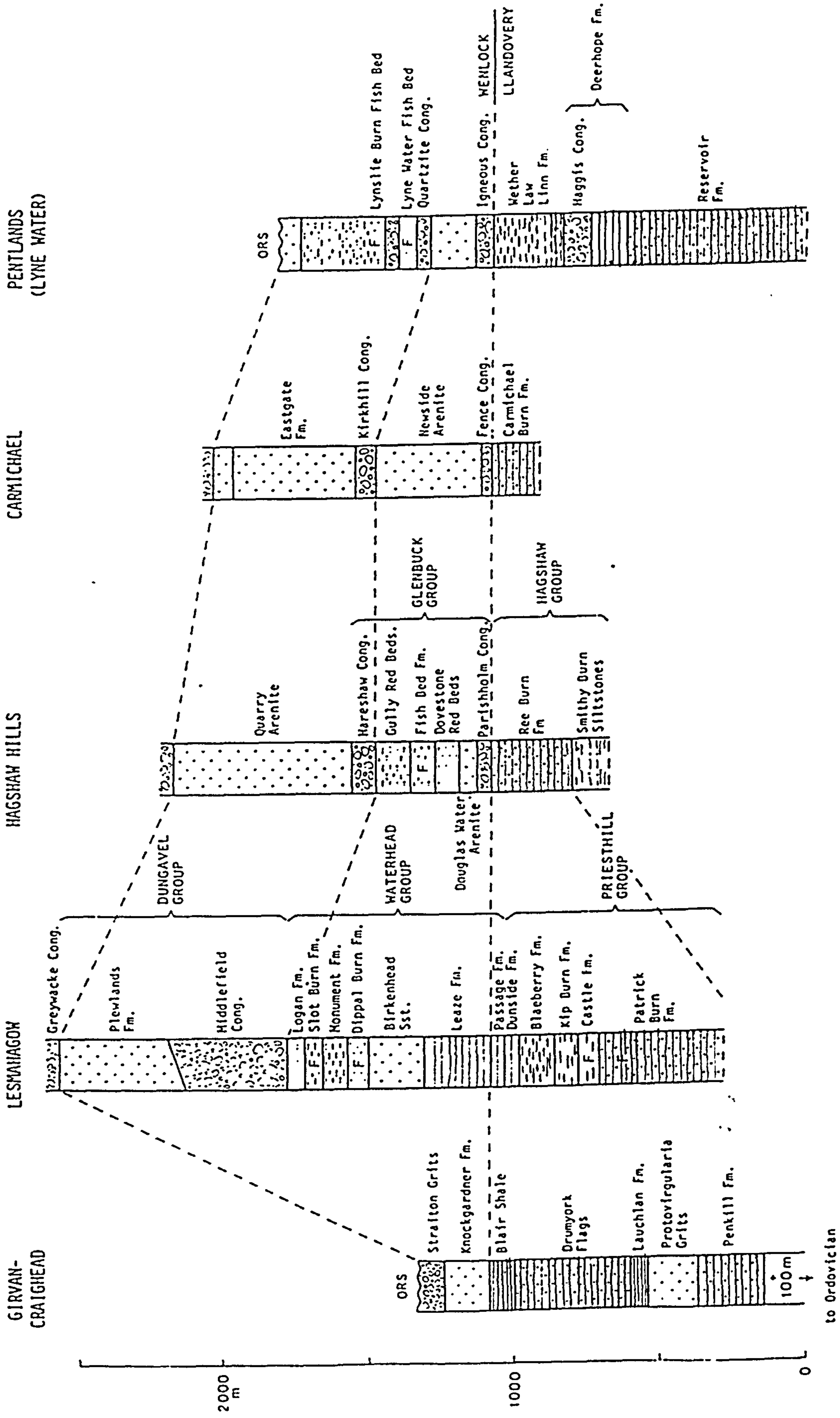
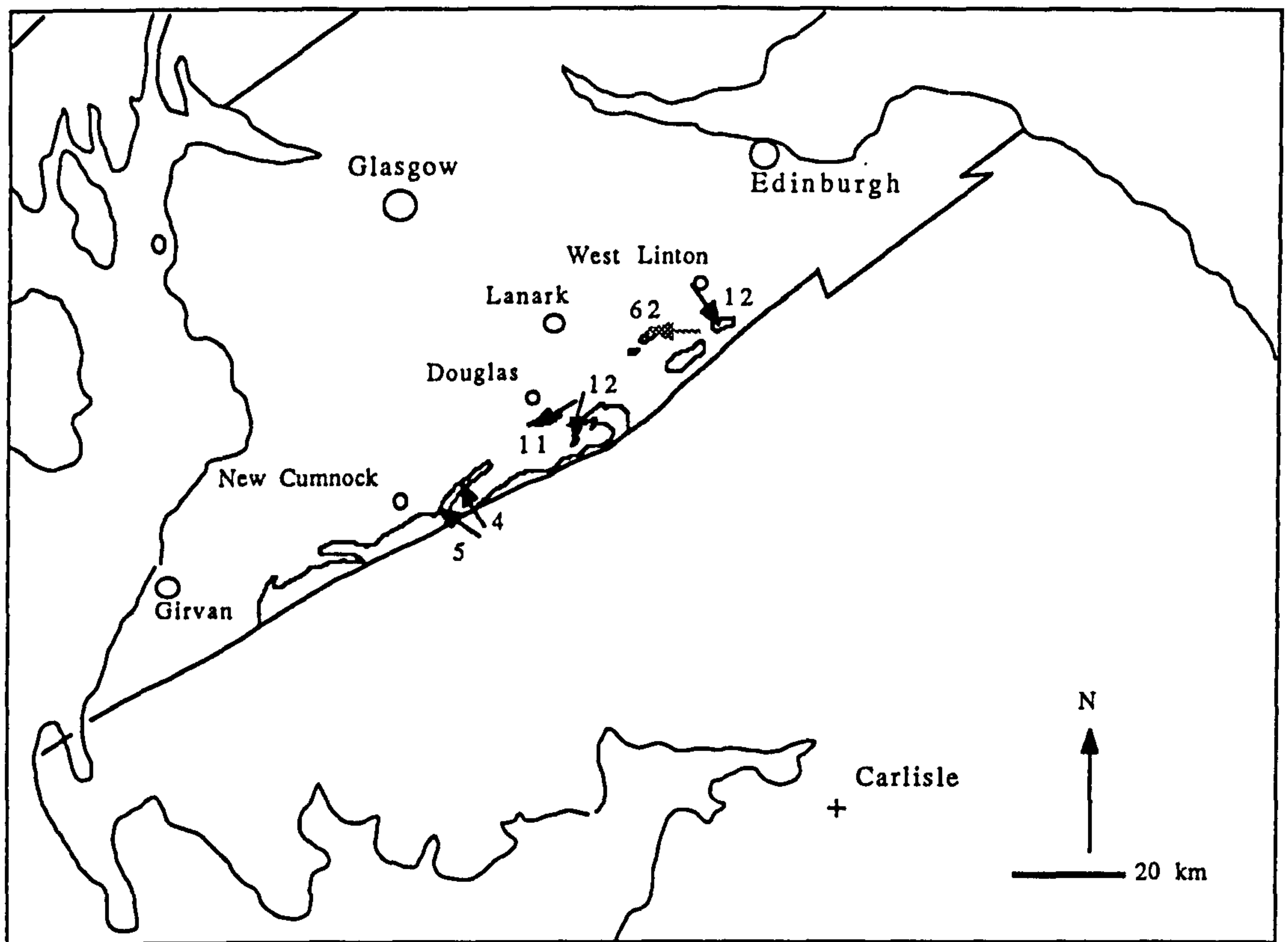


Fig. 2.1 Silurian successions in the Midland Valley. F-Fish beds. Taken from McGiven, 1967.

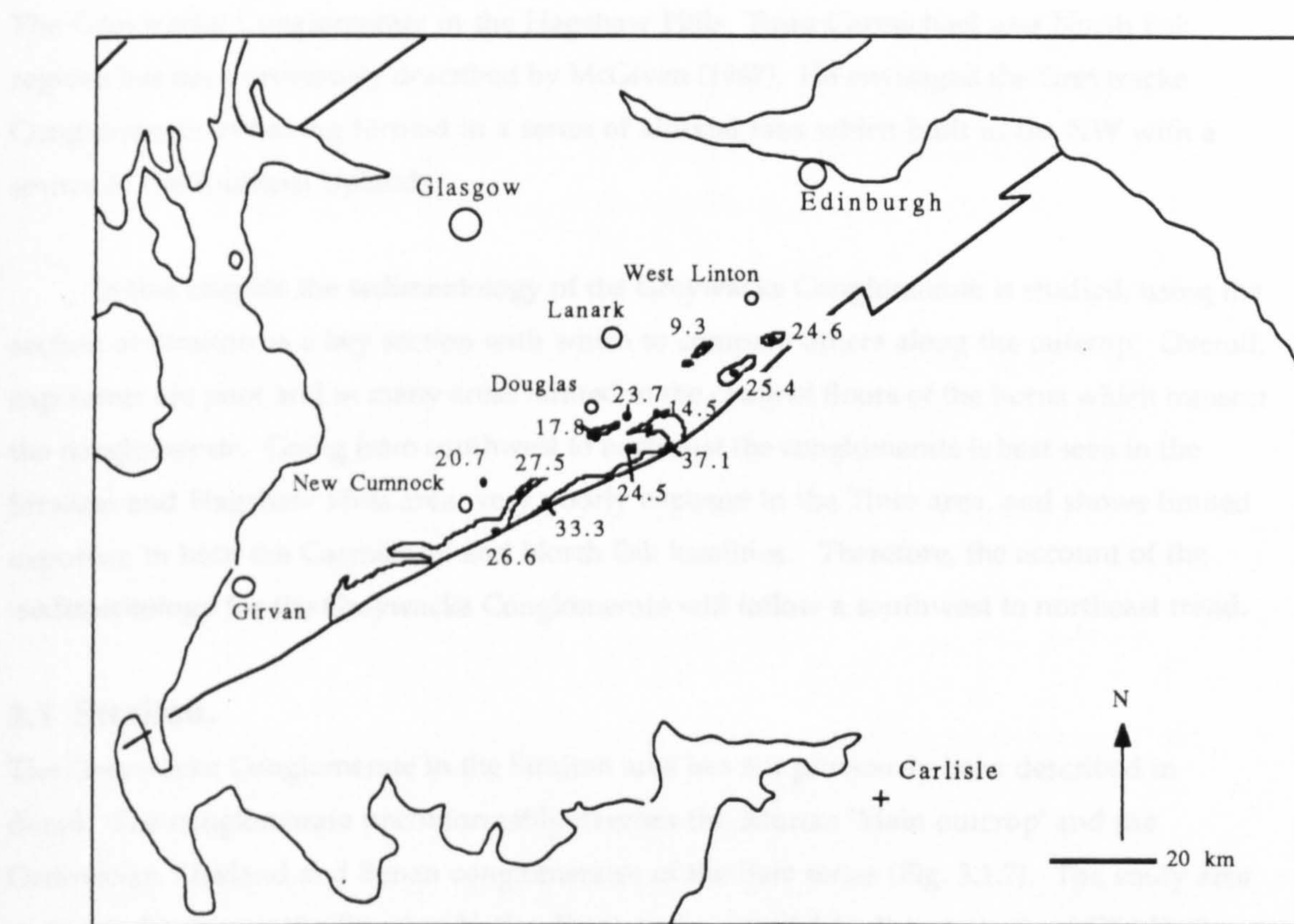


- ← x-bedding in pebbly cong.
- ← imbrication
- 5 number of observations



Fig. 2.2.1 Palaeoflow vectors for Old Red Sandstone Lava Conglomerate.

2.2.2 Distribution of the Lava Conglomerate



• 33.3 Mean Maximum Clast Size



Fig. 2.2.2 Mean MCS in Lava Conglomerate

3.0 Sedimentology of the Greywacke Conglomerate

The Greywacke Conglomerate in the Hagshaw Hills, Tinto-Carmichael and North Esk regions has been previously described by McGiven (1967). He envisaged the Greywacke Conglomerate as having formed in a series of alluvial fans which built to the NW with a source in the Southern Uplands.

In this chapter the sedimentology of the Greywacke Conglomerate is studied, using the section at Straiton as a key section with which to compare others along the outcrop. Overall, exposures are poor and in many areas limited to the channel floors of the burns which transect the conglomerate. Going from southwest to northeast the conglomerate is best seen in the Straiton and Hagshaw Hills area, very poorly exposed in the Tinto area, and shows limited exposure in both the Carmichael and North Esk localities. Therefore, the account of the sedimentology for the Greywacke Conglomerate will follow a southwest to northeast trend.

3.1 Straiton.

The Greywacke Conglomerate in the Straiton area has not previously been described in detail. The conglomerate unconformably overlies the Silurian 'Main outcrop' and the Ordovician Kirkland and Benan conglomerates of the Barr series (Fig. 3.1.7). The study area is situated between the Stinchar Valley Fault and a parallel fault just south of Old Daily, approximately 5 km north of the Stinchar Valley Fault. A series of faults parallel to the Southern Uplands Fault and including the Stinchar Fault cuts the Old Red Sandstone. However, in the northwest of the studied area the Old Red Sandstone overlies one of these faults indicating that at least some of these faults were active before deposition of the Lower Old Red Sandstone. Small outliers located south of the study area on Auchensaul Hill (NX 265945) and near Balligmorrie (NX 230907) suggests the outcrop of the Lower Old Red Sandstone Greywacke Conglomerate and associated sandstones was much more extensive than present day exposures.

In the Straiton area there are two distinct facies sequences, the sandstone facies sequence and the conglomerate facies sequence. The sandstone facies sequence is restricted to sand dominated facies deposits whereas the conglomerate facies sequence is restricted to gravel-cobble dominated facies deposits. Within each facies association a number of lithofacies units occur which together make up the structure of the associations and are considered to be environmentally related (Reading, 1986). The lithofacies units are characterized by specific features, *i.e.* bedding, composition, colour, sedimentary structures, *etc.* in which the fossil biota is not an important constituent of the unit. The features which describe the lithofacies are a product of sediment transport whether erosional or

depositional.

3.1.1. The sandstone facies sequence.

The sandstone facies sequence is the basal sequence of section 2 (Fig. 3-B). The individual lithofacies are described from limited exposure in the N-S trending burn below Doubty Farm (NS 326976). The burn is on average 3-4 m wide and in many places covered by recent gravels. The lithofacies can be accurately described using the facies code of Miall (1978, table 1).

1.) Horizontal laminated sandstones, Sh. Horizontal laminated thinly bedded sandstones are the most frequent lithofacies in the sandstone sequence. The bedding is generally < 30 cm and commonly only 15 cm and although horizontal laminations are characteristic, parting lineation was not observed. Erosional features are notably absent and basal surfaces are always sharp. Small-scale ripples occur at several horizons on the top of this facies.

The sandstones are typically medium-grained but occasionally grade upward into coarser units with intraformational mudclasts and extraformational clasts on their top surfaces forming inversely graded units. Medium and coarser grained sandstones are commonly white or buff colored but where the facies is fine-grained the colour is more typically red. Extraformational clasts include pebbles of well rounded red sandstones, subangular chert, and vein quartz and occur sporadically throughout both the inversely and normally graded beds. The pebbles are typically less than 5 cm but 10 cm clasts of sandstones have been documented.

2). Plane cross-bedded sandstones, Sp. Solitary plane cross-bedded sandstones occur repeatedly throughout the section (plate 3.1). The cross-bedded units range from medium-grained to very coarse-grained but are predominately medium-grained. The average cross stratal thickness is 22 cm and the average angle of the cross-strata is 18°. The cross-beds have tangential toesets but only extend laterally a few centimeters and are overlain by an erosive planar surface. Thin (1-2 cm) very fine siltstone and mudstone foreset drapes have been recorded in one instance. In contrast to the horizontal laminated sandstones the cross-bedded members are always white or buff in colour, probably owing to their coarser grain size.

3). Mudstone and siltstone, Fl. Red and white mudstone and siltstone layers ranging in thickness from 1 cm to 15 cm occur throughout the profile. The siltstones are generally thicker than the mudstones (5-15 cm) and only reach their maximum thickness near the top of the profile where sand infilled dessication cracks are observed. Here they are very thinly bedded and the presence of mica probably accounts for the fissility of this unit. The Fl facies

is commonly associated with the horizontal laminated sandstones and red and white rip-up clasts that occur throughout the Sh facies suggest the fine-grained sediments were more widespread than present day exposures.

4). **Pebbly sandstones, Sm.** Rare massively bedded pebbly sandstones occur in the sandstone sequence. A number of extraformational clasts have been recognized and include i). red-grey sandstone, ii). chert, iii). vein quartz, iv). siltstones and v). green altered pebbles of unknown origin. Erosional features are again notably absent and graded bedding is very rare where only one pebbly horizon with mud and siltstone clasts near the base was seen to grade upward into coarse and medium sandstone. However, as noted above, exposure is limited to 3-4 m, the width of the burn, and it is possible that erosional channels would not be recognized on this scale.

5). **Interpretation of the facies association.** The Sh facies is the dominant facies in the sandstone association. The presence of pebbles and clasts up to 10 cm scattered in the Sh facies suggests the sandstones were deposited by flows also capable of transporting these clasts and therefore in the upper flow regime. The inversely graded units and concentration of clasts on the top surfaces probably result from late stage fallout during waning flow after a major flood event. Rippled surfaces would also be developed during waning flood waters by low velocity flow over previously deposited high energy sandstones. Throughout the lithofacies, siltstone and mudstone rip-up clasts are present indicating the development and erosion of floodplain deposits after and during major flood events.

The Sp facies consists of solitary planar cross-bedded sandstones which occur as isolated structures within the Sh facies. Palaeoflow measurements show a unimodal direction of dip of the foresets indicating a single migration direction of the bedforms. The facies is always overlain by horizontal erosional surfaces and resemble the transverse bars of Smith, N. D. (1971, 1974), cross channel bars of Cant (1978), and simple bars of Allen (1983). Reactivation surfaces are not present and the isolated nature of the Sp facies suggest the sandstones were deposited as single non-repetitive units, since repetitive migration of bars would give rise to stacked Sp facies. The relatively low angles, average of 20°, are considered low for development of avalanche foreset deposits. Smith, N. D. (1972) records an average foreset dip angle of 23.7° for dunes and larger angles for diminished dunes and ripples. The lower angles of foreset deposits in the sandstone sequence could be a function of either outcrop exposure or compaction. Smith (*ibid*) suggests that angles significantly less than the angle of repose could result from the shifting of depositional strike on irregularly shaped bars. Outcrop exposure is not laterally extensive enough to evaluate this possibility.

Although, solitary planar cross-strata are usually associated with in-channel bars McKee *et al.* (1967) recorded planar cross-strata in floodplain deposits of the Bijou Creek, Colorado. They do not record an angle but classify them as low to moderate angles produced by a deepening of flood waters.

Erosion and scour surfaces are absent in the sandstone sequence and this could be interpreted as either channels were not present or at the scale of outcrop too small to recognize them. If channels were present then the presence of basal conglomerates overlain by cross-bedded, trough and/or tabular, sandstones and eventually filled with fine-grained siltstones or mudstones would be expected. Tunbridge (1984) records channel filled sandstones with an intrabasinal conglomerate followed by a single set of cross-stratified sandstones and directly overlain by parallel laminated sandstones in sandy ephemeral streams. In many cases, the basal conglomerate is directly overlain by parallel laminated sandstones. In the sandstone sequence a few pebbly sandstones are present but none of the coarser units are overlain by typical deep-channel bedforms associated with channel infills, *e.g.* trough cross-bedding. The coarser units which are themselves quite massive are invariably followed by plane-laminated sandstones. Without the erosional surfaces it is hard to say whether the conglomeratic beds are true channel features equivalent to those recorded by Tunbridge (*ibid*).

McKee *et al.* (1967) recorded a predominance of parallel laminated sandstone over all other sedimentary structures in the flood deposits of Bijou Creek, Colorado. Williams (1971) in his study of channel flood sands in ephemeral streams in central Australia concluded that plane laminations with parting lineation accounted for only 5% of deposits. Upper flow plane-laminated sands were confined mainly to longitudinal bars or shallower parts of channel beds. This facies was the dominate structure only in the middle reaches of the Finke River, Australia where maximum flood waters were recorded.

The dominance of horizontal laminated sandstone, absence of trough cross-strata and erosional features, presence of thin mud-siltstone layers interbedded within the sandstone suggests the sequence was deposited as sheetfloods in ephemeral streams. If channels were developed the implication of the observed sedimentary structures suggests that the channels would have been broad and quite shallow. The average thickness of the individual lithofacies including cross-stratal thicknesses supports this conclusion. Sand bars may have been active in these shallow channels giving rise to the Sp facies. The mudstone drapes associated with the Sp facies at one locality suggests that the suspended sediment was deposited in abandoned pool slough-channels during receding flood waters, (*cf.* Bluck, 1974). The Fl facies in the majority of the sandstone sequence directly overlies the Sh facies. The Fl

facies was probably generated by rapid fallout in either a broad channel floor or on the more elevated floodplain.

6). **Vertical arrangement of facies.** The vertical arrangement of the facies (section 2, Fig. 3-B) shows an overall upward fining of the sandstone sequence. The top 7 m of the sequence is composed solely of fine-grained sandstones, siltstones, and dessicated mudstones. The fine-grained nature could be in response to an overall change upward to a more distal facies or could represent a shifting of the main channel. The uniformity of the sequence below the upper Fl facies suggests the upper fine-grained sediments were in response to an eventual filling of major/minor channels associated with shifting of the main channel. It is noticeable that within the finer-grained facies soft sediment deformation is absent. It could be that the water table was never high enough to fully saturate the sands. The strike of the small-scale ripples within the upper 7 m is nearly perpendicular to the mean direction of cross-strata. This indicates that the ripples were formed in relatively quiet water conditions possibly in a slough channel.

3.1.2. The conglomerate sequence.

The conglomerate sequence is much more extensive than the sandstone sequence and exposure can be seen in a series of hilltop ridges as well as in the burns. Conglomeratic units comprise 70-100% of the beds in the conglomerate sequence. Three distinct lithofacies can be recognized in the sequence: i). a massive structureless conglomerate, Gm1, ii). a well imbricated horizontally bedded conglomerate, Gm2, and iii). planar cross-stratified conglomerate, Gp. Of the three lithofacies Gm1 and Gm2 are by far the most common with only one occurrence of the Gp facies. Minor occurrences of trough cross-stratified pebbly conglomerates have also been noted.

1). **Massive structureless to crudely organized conglomerate, Gm1.** The Gm1 facies is described from limited exposure in the burns which cross-cut the conglomerate sequence. The conglomerates are composed of rounded to well rounded clasts of sandstone and minor amounts of cherts, with rare quartzites and volcanics. The conglomerates are either clast-supported with a matrix of medium-coarse sand or rarely matrix-supported. Open framework conglomerates are very rare, only one example of a calcite infilled conglomerate was recorded in a fine-grained conglomerate. Large-scale erosional and scour features are noticeably absent. In one instance, very small scale scouring, less than 15 cm, was seen, the scour feature itself filled with conglomerates. Basal contacts are, in general, very difficult to recognize but when seen are always planar, with the one exception above. Bedding thicknesses range from 15 cm to 87 cm and the mean bedding thickness is 40.6 cm with a standard deviation of 17.9 cm (Fig. 3.1.1a). The Gm1 facies, this study, would be equivalent to the type 1 facies of McGiven (1967).

Clasts within the Gm1 facies, calculated from the same beds from which bedding thicknesses were determined, range from 3.4 cm to 17.9 cm (a-axis length) with a mean of 9.3 cm and a standard deviation of 3.8 cm (Fig. 3.1.1b). Roundness values from the clasts within the conglomerate are very high with nearly all the clasts lying in the well rounded to rounded category of Pettijohn, (1975 table 3-9, p. 57). In general, imbrication is lacking and the predominance of spherical or rod shaped clasts in the Gm1 facies can account for the poorly imbricated conglomerates (see Rust, 1975). Imbrication is recorded only from isolated clusters of clasts, 2 to 3 clasts per group cluster, which show b-axes orientated perpendicular to the dip of the clast. A small number of the larger clasts are graded but the majority of the clasts are thinly laminated especially in the finer-grained varieties. Sorting of the clasts within the Gm1 lithofacies is generally poor, clasts are randomly organized and vertical clasts are common. Histograms measured on clast sizes ≥ 1 cm in 1/4 sq. metre are shown in Fig. 3.1.2. It can be seen that the Gm1 facies conglomerates are poorly sorted with the majority of clasts falling in the 0-5 cm category but also containing clasts up to 17.5 cm. Sorting in the Gm1 facies generally improves upward through the section with a slight decrease near the top.

The conglomerates generally lack internal stratification. However, the conglomerate beds can show a repetition of fine and coarse conglomerates at outcrop level. The change from a poorly-sorted massive conglomerate (plate 3.2) to moderately-sorted, finer-grained conglomerate (plate 3.3) occurs both vertically and laterally. In vertical profile the fine-grained unit always overlies the more massive conglomerate. In some cases, the bed boundaries are well defined and sharp whereas in others marked textural changes are clearly transitional. The bedding thicknesses associated with this crude organization range from 20 cm to 1.3 m and there does not appear to be a significant variation in bed thickness between the poorly-sorted coarse conglomerates and the finer-grained conglomerates. Compared to the coarser the finer grained conglomerate shows a slight improvement in sorting but outsized clasts are ubiquitous. Both units have a bimodal texture with a sand matrix, although in the finer conglomerate this matrix is much reduced.

The conglomerates occasionally grade upward into a thin (c. 5 cm) medium-grained sandstone top (plate 3.4) which when traced laterally in the downstream direction overrides the conglomerate forming a sharp contact between the two. Thin medium to coarse-grained sandstone beds also occur as discrete sandstone units. The sandstone beds are either flat-stratified or show very low-angle, less than 10° , cross-bedding. The conglomerates may also fine upward by increasing medium-coarse sand matrix into a sandy conglomerate (plate 3.5) where the clasts are supported by the sand matrix. The clasts themselves do not show a decrease in mean maximum clast size in the sandy conglomerates when compared to the coarser clast-supported conglomerates.

Only in one case were very fine-grained sediments associated with the Gm1 facies, a very thin 2-3 cm sheared mudstone located between a conglomerate-sandstone couplet. Where exposure permits the conglomerate beds, with or without sandstone tops, cannot be traced for more than a few metres before amalgamation with overlying or underlying conglomeratic units.

Relatively thick (c. 2 m) fine-grained flaggy and massive coarse-grained sandstones are interstratified with the Gm1 facies. The fine-grained sandstones form discrete units with sharp contacts but the coarser sandstones are seen to occasionally grade upward into sandy conglomerates.

2). **Horizontally bedded or stratified conglomerates, Gm2.** The Gm2 facies is mainly described from ridges exposed along Doubty Hill (NS 324978), plate 3.6. A much smaller percentage of this facies is found in the burn sections. As a consequence of the exposure, lateral trends within the Gm2 facies can be delineated.

The conglomerates within this facies are clast supported with a coarse to very coarse-grained sand infilled matrix; open framework and calcite infilled conglomerates are absent. Compared to the Gm1 facies the Gm2 facies is thinner bedded, mean bed thickness 31.4 cm, and has a much lower bedding thickness standard deviation, 8.6 cm, (Fig. 3.1.3a).

The clasts within facies Gm2 are more angular than the clasts in the Gm1 facies (plate 3.7) with the majority of the clasts falling into the subangular to subrounded class of Pettijohn (1975). In contrast to the the Gm1 facies, the Gm2 facies has a smaller average maximum clast size, 8.0 cm, and lower degree of variation about this mean, 1.9 cm, (Fig. 3.1.3b). The clast shape is commonly discoidal, rod-shaped and spherical in descending frequency. Sorting histograms, measured on clast sizes ≥ 1 cm in 1/4 sq. metre, are shown in Fig. 3.1.4. and it can be seen the degree of sorting is higher in the Gm2 then in the Gm1 facies. Outsized clasts are rare in this facies. Imbrication (b-axis) is widespread and can be quite variable with up to 90° divergence in a single bed (Fig. 3.1.5).

Very thin bedding with sharply defined contacts between conglomeratic units is characteristic of the Gm2 facies. These contacts are especially well defined where the conglomerates grade upward into thin (c. 5 cm) medium-grained sandstone tops. The sandstone tops are better sorted and finer-grained than the matrix associated with the corresponding conglomerate and may themselves be normally graded from coarse-grained sand at the bottom to medium-fine grained sand at the top. Similar to the Gm2 facies the sandstones are either horizontally laminated or show very low-angle, c. 5° or less, cross-

bedding. The sandstone tops thicken in the direction of palaeoflow and can be laterally traced for approximately 2 m before they die out. The tops of some conglomerate units may not develop true sandstones but instead grade upward into sandy conglomerates. Small isolated lenses of sandstone with both concave bases and convex tops which laterally thin in the direction of palaeoflow occur in the facies (plate 3.8).

Like the Gm1 facies large-scale erosional features are absent but small-scale scour features are present. Conglomerates can be seen to scour into the underlying bed of both the normally graded sandstone topped conglomerate and non-graded conglomerates.

The conglomerate beds can be traced laterally for only 3-4 m before the conglomerates coalesce and bedding is no longer discernible. In a few instances the beds have a concave structure where along the edges the beds thin to only 1 clast thickness before amalgamation with the underlying bed, this change in thickness can happen in less than 2 m.

3). Planar cross-bedded conglomerates, Gp. Only one example of planar cross-stratified conglomerate was seen. The conglomerates were poorly sorted, clast-supported with foreset inclination approaching the angle of repose, *c.* 30° (plate 3.9). The cross-stratal thickness is in excess of 0.6 m, the base of the unit was not seen. Horizontally stratified poorly-sorted, clast-supported conglomerates, Gm1 facies, formed the planar erosive top surface to the cross-bedded unit. Palaeoflow directions taken from isolated imbricated clusters in the Gm1 conglomerates are at a high angle to the planar cross-strata.

4). Trough cross-stratified conglomerate, Gt. Only one example of trough cross-stratified conglomerate was seen. The conglomerate is intimately associated with trough cross-stratified pebbly sandstones (plate 3.10).

5.) Interpretation of facies Gm1, and Gm2. Both the Gm1 and Gm2 facies are characterized by horizontally bedded cobble conglomerates. The main difference between the two facies is the development of imbrication, lower degree of roundness, thinner bedding, and higher percentage of disks in the Gm2 facies.

Hein and Walker (1977) studied the active development of bars during flood discharges in the Kicking Horse River, British Columbia. The authors showed that in the upstream reaches the gravel moved as diffuse sheets only 1 to 2 clast size thick and extend the width of the entire channel. The diffuse sheets or lag gravels evolve into unit bars; diagonal, longitudinal or transverse bars, depending on the sediment and water discharge. High sediment and fluid discharge favour downstream growth giving rise to longitudinal and diagonal bars where high-angle foresets are uncommon but low-angle stratification in the

downstream direction may be present. Alternatively, low sediment and fluid discharge would result in the development of transverse bars with high-angle foresets by vertical aggradation.

N. D. Smith (1974) studied the evolution of the unit bars, newly formed gravel bars with a simple shape whose morphology is determined solely by deposition, in the Kicking Horse River. The shape of the unit bars; longitudinal, transverse, diagonal, and point bars depend on the conditions of flow variables, channel geometry and bank stability. Longitudinal bars form where flow strength is equal, channel morphologies is symmetrical, and flow is unidirectional on opposite sides of the bar. In contrast, diagonal bars form where flow is asymmetrical, *e.g.* channel bends, channel junctions and downstream from exposed braid-bars. Transverse bars are typical of areas where flow lines diverge by channel widening or a sudden increase in depth. Point bars form only in conditions similar to meandering streams, erodable outer margins in the bends of channels. Smith concluded that after subsequent vertical and lateral aggradation unit bars would eventually become exposed and later erosion and deposition would obscure the relatively simple internal and external geometry of the unit bar. Therefore, unit bars would not be expected to be represented in the ancient record, instead a complex bar produced by both erosional and depositional processes would be preserved.

The thinness of the Gm2 beds and lack of large-scale erosional features suggests the conglomerates were deposited by shallow unconfined flows. The lack of cross-stratification associated with the Gm2 facies precludes the development of transverse, and point unit bars and would indicate that stable bars were not present. The Gm2 facies resembles the longitudinal or diagonal unit bars of Smith (*ibid*) where the bars thin and fine both vertically and in the downstream direction. This suggests the bars were developed from high water and sediment discharge.

The fact that the bars cannot be traced in either the downstream or cross-axis direction for any length suggests the bars were of a very small size. Large-scale longitudinal, and diagonal bars were probably never developed in the Gm2 facies. Complex coarsening upward assemblages, coarse bar heads migrating over finer tails, recorded from braid bars by Bluck (1980b, 1982, 1986b) are absent in the Straiton conglomerates. This would indicate that stable bars capable of migration in the downstream direction were not present.

The simple geometry of the Gm2 facies imply that the bars were not subjected to extensive modification after recession of the flood waters when the bars would be exposed. Variations of palaeoflow within the Gm2 facies (Fig. 3.1.5) are believed to be produced by small diagonal unit bars. Imbrication of clasts between beds can diverge by as much as 90-

100°. There is no change in maximum clast size between the longitudinal bars and the beds which have a high degree of divergence to mean flow. The diagonal bars must have been produced when flood waters were channelled back into the shallow channels which separated the unit bars. Lateral accretion surfaces with relatively high angle foresets are not present in the diagonal bars. Hein and Walker (1977) show that foresets were absent in the diagonal bars and produced mainly from lateral accretion in an asymmetrical flow. Using data of N. D. Smiths (1985) who calculated that flow depth/ grain size ratio must be greater than 10 to produce planar cross-strata, Morrison and Hein (1987) concluded that stratified gravel similar to the Gm2 facies were deposited in flows with an average depth of 0.9 m. Similarly, the mean maximum clast size of the Gm2 facies is 8 cm and would produce slipface foresets only if the flow depth was greater than 80 cm. The corresponding mean bedding thickness associated with the 8 cm mcs in the Gm2 facies is only 31.4 cm and would thus indicate the flow depth over the top of the unit bars was probably considerably less than 80 cm.

The absence of sandstone drapes (*cf.* Ramos and Sopena, 1983) and well developed imbrication indicate that flow conditions did not change significantly during the falling flow stage. Changes in flow orientation during low-stage flows are dependent on bed relief. Instead, the low relief of the bars along with a slight decrease in the flow height of the shallow floods were probably sufficient to transport even the coarsest bedload at a high angle to the mean flow direction.

The dominance of coarse gravels and paucity of sandstone units is thought to be a function of availability of sand sized particles in the source area. The majority of sandstone cappings do not show erosive features on their top surfaces but instead are sharply overlain or grade into the overlying conglomerate. Where scouring of the sandstones is observed the level of erosion is less than 5 cm and would augment the argument that most of the sand-sized deposits have been left intact during subsequent floods. The grading in the sandstone caps, finer grained size and higher degree of sorting when compared to the matrix indicate that sand sized particles in suspension were vertically aggraded during final low flow stage. Lateral aggradation as well as vertical aggradation was still an important mechanism of sediment transport during low flow stage as evidenced by very low angle cross-stratification in the sandstone cappings and thickening away from palaeoflow.

The coarse to granule sized material forming the majority of the matrix was probably carried in suspension and settled at approximately the same time as cessation of cobble movement. A mechanism of matrix infiltration similar to the process recorded by Rust (1984), where at high froude numbers the suspended sand can penetrate to maximum depth (the

entire thickness of the beds), was probably the most likely origin of the matrix. It has already been noted that the conglomerates were deposited in high velocity, low depth flows which would equate to high froude numbers.

Sandstone lenses (plate 3.8) which occur infrequently in the Gm2 facies are probably the product of low flow stage tractional sedimentation. The poorly sorted coarse-grained sandstone lenses thin in the opposite direction from palaeoflow. The sandstones occasionally formed topographic features as overlying conglomerates thin over the crests and thicken in the troughs. The sandstone lenses sharply overlies the sandstone cap of the sandstone/conglomerate couplet and pinch out in the direction of palaeoflow. The sandstone is indistinguishable from the matrix of the conglomerate facies. All these features suggest that deposition of suspended sands was initiated by slight deepening of flow in hollows formed possibly by turbulence in the lee of unit bars. Once deposition was initiated the sandstone lense was modified into a small bedform which produced a topographically high feature.

Occasionally the discrete sandstones can be traced laterally in the upflow direction into conglomerates. These sandstone lenses may have formed from separation of fine material in the tail region by accumulation of sand in the lee of the head region (*cf.* Bluck, 1980b). However, the sediments differ from Bluck's facies in two important aspects; 1) cross-strata is not developed in the sandstones and 2) interfingering of sandstones and conglomerates does not occur. The absence of cross-strata would indicate that there was very little difference in height between the bar head and the bar tail. The contact with the overlying conglomerate is mainly abrupt but small scale scouring of the sandstone lense is present indicating two distinct phases of sedimentation.

The total absence of material finer than fine-sand including mudstone intraclasts common in sandy sheetflood deposits (Allen, 1983; Tunbridge, 1981) and recorded in conglomeratic deposits (Ramos and Sopena, 1983) is thought to be due to: i) true braided channels were not developed and consequently abandoned channels with slough fill fines did not evolve, ii). high flow velocities (strong enough to move fine-medium sand in the downstream direction during waning floods) were too strong to allow settling of very fine to mud particles and, iii) absence of elevated floodplains.

In contrast to the Gm2 facies above the Gm1 facies has very limited exposure and as such cannot be traced laterally for any length. Within the clast-supported Gm1 facies two subfacies can be recognized, a coarse texturally immature conglomerate and a finer, texturally more mature conglomerate. Steel and Thompson (1983) have described a similar fabric organization in the Triassic Bunter Pebble Beds. The authors have interpreted the repetition

of the two subfacies as a lateral progradation of size segregated bars. This would produce a repetition of fine gravels (bar-tail) coarsening upward into coarse gravels (bar-head), a process very similar to observations by Bluck (1979, 1986b). The lack of lateral control on the Straiton conglomerates does not enable the coarsening upward trend to be verified in most cases. One case does show a lateral transition but instead of being downcurrent from the main flow is at a high angle to palaeoflow. This could be a consequence of size segregation along the sides of the bar as well as in the tail region similar to Boothroyd and Ashley (1975) where the authors record the coarsest material in the centre of the bar. The total absence of tabular or trough cross-bedding associated with the size segregated units would again preclude the development of stable bar forms with slip faces.

Local calcite infilling of the finer material implies that matrix was absent during or subsequent to the deposition of the finer material. Open framework fabric in gravel beds have been recorded by Steel and Thompson (1983) and interpreted as winnowing of fines during falling flow stages. With falling flow stages the coarser middle portion of the bar may have emerged to form a topographic high. Finer gravel could still be in tractional transport along the sides and in the tail region. Turbulence in the lee of the topographic high could be responsible for local removal of sand sized material to produce open framework gravel.

The development of size-segregated units is not a widespread phenomenon and the massive structureless clast-supported conglomerate is more typical. These conglomerates are characterized by a high concentration of sand sized matrix, poor degree of sorting, and total absence of internal stratification and imbrication which resemble the sediment-charged sheet flows of Ballance (1984, facies 3) and Morrison and Hein (1987, facies 2 and 3). Sediment-laden fluid flows or hyper-concentrated fluid flows, Smith, G. A. (1987), have properties which are intermediate to both debris-flows (cohesive-plastic behaviour) and fluid-flows (cohesionless-fluid behaviour). The deposits produced by such flows are poorly-sorted, clast-supported, normally graded and may have a-axis imbrication, Smith, G. A. (*ibid.*). Gloppen and Steel (1981) describe identical deposits to Smith except normal grading is absent. Instead, the beds may be inversely graded. Imbrication is lacking and replaced by high angle fabrics, e.g. vertical clasts. The authors attribute these deposits to true debris-flow mechanisms where matrix strength and laminar flow are responsible for the above textural characteristics.

Debris-flows in the literature refer to both a matrix-support mechanism and sediment-support mechanism. Lowe (1979) suggest the terms cohesive debris-flow for flows which exhibit plastic behaviour and have a matrix-support mechanism. In contrast, grain-flows are flows which behave plastically but dispersive pressure is the main sediment-support. In this

sense most sediment-laden fluid flows described in the literature do not contain the necessary "mud" constituents, clay to fine-sand sized particles, to produce a true cohesive debris-flow. Instead, dispersive pressure sediment-support, supplied by the dispersion of grains by collision against gravity, is a more fundamental process. Therefore, the sediment-laden fluid flows show a similarity in support mechanism to Lowes grain-flow. However, sediment-laden fluid flows are probably not strictly behaving in a true laminar flow but instead as flow transitional between laminar and fully turbulent.

The Gm1 facies have features which could be interpreted to represent flows transitional between laminar and turbulent and defined as sediment-laden fluid flows. The Gm1 facies is totally lacking in material finer than fine sand and would therefore negate the origin of the sediment from true cohesive debris flows. The disorganized clast-supported fabric in which large clasts are frequently vertical suggest rapid deposition of the unit as a whole. Maximum clast size versus bed thickness plot of the Gm1 facies (Fig. 3.1.6a) shows a positive correlation. Nemec and Steel (1984) point out that a positive linear correlation between bed thickness and maximum clast size (average of ten largest clasts) has been cited by numerous authors suggesting debris-flow or mass-flow mechanisms. Bluck (1967) defined this relationship as recording the positive correlation between the competence of the flow (mcs) relative to the sediment discharge (bth). In turbulent flows this relationship fails due to i). sediment is being deposited at the same time as sediment is being transported and, ii). erosional processes which can seriously obscure the original sediment discharge.

The Mcs/Bth for the Gm1 facies diagram (Fig. 3.1.6 a) shows that even though there is a significant linear positive correlation, $r=0.72$, the F test on the analysis of variance for simple linear regression shows that a fitted straight line does not closely approximate the data. Poor fit may arise from a high variance in the dependent variable, Davis (1986), in this case Mcs. This would imply that for a given bed thickness competence of the flow measured by maximum clast size varies significantly in the Gm1 facies. It may be that in the sediment-laden fluid flows the transportation of at least some of the largest clasts is mainly by traction on the floor of the substrate. Lowe (1979) describes tractional transport of large clasts in debris flows and concludes that rheologically debris flows can include both tractional and suspended sediments. The loss of tractionally transported clasts by obstructions, possibly by large clasts incapable of being moved by the flow, would result in an increase in the turbulence of the flow and subsequent modification in the flow competence by either deposition and or erosion. This may account for the variation in Mcs with respect to Bth. The fact that most of the imbrication developed in the Gm1 facies is found only in small clusters of some of the largest clasts supports the conclusion that traction did play an important part in the transportation of the larger clast fraction.

Bth/Mcs for the Gm2 facies also shows a significant positive correlation, $r = 0.70$, (Fig. 3.1.6b) again indicating cohesive flow. Variation about the dependent variable, mcs, is higher than in the Gm1 facies indicating tractional transport is more important in the Gm2 facies compared with the Gm1 facies. The transportation of the sediment by turbulent flow cannot be disputed with the widespread occurrence of imbrication in the Gm2 facies. The more important question is why there is a positive correlation between Bth/Mcs. The answer may be that rapid sedimentation of high velocity floods, whether turbulent or sediment-laden, without later modification by erosion may preserve the relationship between competence of fluid flow and sediment discharge.

Normal grading is rare in the Gm1 facies, a feature that is common in the more cohesionless debris flows described by Nemec and Steel (1984) and hyper-concentrated fluid flows described by Smith, G. A. (1986). Normally graded units are typical of flows which result from a turbulent flow. The rare occurrence of sandstone cappings which are commonly plane stratified or show very low angle cross-stratification indicate that during the final stages tractional processes were dominant. When sandstone cappings are present the conglomerates grade upward into the very thin sandstone which laterally sharply but not erosively overlies the conglomerate. While conglomerates were effectively frozen the sands, deposited during the waning flows, moved over the conglomerate. The final flow velocity was incapable of remobilizing the underlying conglomerate.

Inverse grading has been recorded in only one conglomerate but does suggest that dispersive pressure, usually attributed to the formation of inverse grading in conglomerates, may have played a role in the formation of the Gm1 conglomerates. This singular conglomeratic bed may thus be a product of deposition by true debris-flow mechanisms.

In the conglomerates in which sand becomes an important constituent of the unit the bedding in these sandy conglomerates is extremely thin with a mean thickness less than 10 cm. The conglomerates are very poorly-sorted which laterally show minor thinning and separation into coarse sandstone. Associated with these beds was one small scale low-angle trough cross-bedded sandstone. Small scale scouring and erosion are more common in these sandy conglomerates than in the massive structureless conglomeratic units. Imbrication is not a common feature and outsized clast greater than the mean maximum clast size (9.3 cm) of the Gm1 facies are common.

The above features indicate that turbulent flow, at least in the final stages of deposition, was responsible for the present day characteristics of the sandy conglomerates. The overall increase in the sand matrix and thinness of the bedding suggest the flow velocity

and depth responsible for the deposition of the ungraded massive conglomerates more typical of the Gm1 facies had decreased substantially. The presence and size of outsized clasts indicate that at least some of the clasts were lag deposits. The lack of widespread imbrication, cross-bedding and size segregation of the deposits indicate that "true bars" were not developed in the sandy conglomerates. Instead, late stage modification by turbulent flow over the ungraded Gm1 facies seem to be a possible mechanism.

Within the Gm1 facies sandstone does not form a large percentage of the unit. Instead, when "thick" sandstones are present they lie with sharp non-erosive contacts and cannot be traced laterally into the Gm1 facies. The sandstones range from massive to horizontally laminated. They could be formed from i). more quiescent discharges into the basin or ii). "intersurge" deposits following the deposition of the main high velocity flows. The low proportion of sandstone deposits associated with the Gm1 facies is probably due to the lack of available material which is effectively frozen in the coarse conglomerates.

One occurrence of large scale planar cross bedded conglomerate was found. The exposure is poor but horizontally bedded conglomerates can be seen to both underlie and overlie the plane cross-bedded units. The cross-bedding is high angle, 30°, and is at a high deviation to the imbrication measured in the horizontally bedded conglomerates. Alternation of the finer and coarser cross-bedded units described by Rust (1984) and Steel and Thompson (1983) are not recorded in the above unit. The conglomerates were obviously deposited under turbulent flows in what must have been exceptional floods. The mean maximum clast size is 17.4 and exposed cross-bedding thickness, 60 cm, is larger than the average bed thickness in the horizontally bedded Gm1 facies. The formation was probably due to migration of large-scale longitudinal bars. The variation of the palaeoflow indicators, imbrication and cross-bedding, is difficult to rationalize and may represent a change in the palaeocurrent during the exceptional flood.

3.1.3. Vertical and lateral variation.

Measured sections shown in Figs. 3-A and 3-B, localities shown in Fig. 3.1.7, were chosen because more or less complete vertical sections could be studied with respect to facies, maximum clast size, percent sandstone in the conglomerate sequence, clast composition and clast roundness. The vertical sections show the logged sections corrected for regional dip, sills and dykes removed.

Paleoflow rose diagrams are from imbrication (solid vectors; refer to Fig. 3.1.9, Fig. 3-A, *etc.*) and cross-bedding in the sandstones (dashed and grey vectors; refer to Fig. 3.1.9, Fig. 3-B, *etc.*), N equals the number of measurements, X equals the mean palaeoflow direction, L equals the magnitude (measure of the concentration of the azimuths) of the resultant vector in terms of percent.

Percent sandstone was measured from discrete sandstone units in 30.5 metres (100 ft) of exposure. Where exposure is not continuous the frequency of sandstone was recalculated to the fraction of the exposed section in the 30.5 metres.

Maximum clast size measurements were calculated from the mean of the ten largest clasts in one square metre. The square metre was chosen to give the largest mean value in a given area.

Roundness and composition diagrams were calculated from marking out one square metre and collecting 35 clasts from the 0-5, 5-10, 10-15, 15-20 cm categories according to the appropriate size of the maximum clasts at the given locality. The square metre was expanded by another square metre and so on until 35 samples for a given category were collected. This procedure helped to ensure that the sampling procedure was indeed random and clasts with an unusual composition were not chosen above the more common constituents. The selected clasts were visually compared with the roundness chart in Pettijohn (1975 fig. 3.24, p. 57) and placed in the appropriate category. The roundness value was calculated by multiplying the midpoint of each category (Pettijohn, 1975 table 3.9, p. 57) by the number of samples in the corresponding category and calculating the arithmetic mean for the total population.

a). **Facies and maximum clast size variation.** Schumm (1981) showed that the sedimentological characteristics in the depositional site is a direct response to factors affecting both the drainage basin and the transfer zone where material is moved from the drainage basin to the depositional basin. The main factors are outlined in Schumm, 1981 (table 1, p. 21) and include time, initial relief, geology (lithology and structure), climate, hydrology, and relief of system above base level.

It has been argued that the coarse-grained sediments in the Gm (1 & 2) facies are a product of high sediment and fluid discharge and as such most of the material was transferred to the depositional basin as bedload and deposited very rapidly. These conditions are usually in response to young fluvial systems, and dry climates where initial relief is high.

The most noticeable feature of the conglomeratic sequence is the similarity of the succession from the base to the top and the absence of mature bars and suspended load sediment. The lack of vertical variation in the facies can be adequately explained if climate (dry with high intermittent peak sediment and fluid discharge), geology of the source block and relief of the drainage system relative to the base level remained relatively constant

with respect to time. As seen from area diagrams of the composition of the clast lithologies (Fig. 3-A, 3-B) erosion into the source region did not encounter any major change in the geology. With time it would be expected that degradation of the uplifted block would lower the gradient of the base level and changes in the basin of deposition would become pronounced. To account for the absence of morphological changes a steady rate of subsidence in the depositional basin or a steady rate of uplift would have to play a major role in the deposition of the conglomeratic sequence.

Comparison of Figs. 3-A and 3-B shows a consistently coarser grain size in the conglomerate sequence in section 1. The coarsest material is not located at the base of the conglomerate but at approximately 25 metres above the base in section 1 and 15 metres above the base in section 2. The maximum clast size in both cases is at a significantly coarser grain size relative to the rest of the section to assume that both can be correlated and represent the dynamic influx of material into the basin. Although this assumption is likely to be made strictly on sedimentological features it will be shown in later chapters that correlations cannot be made between the two sections. It is significant that the base of the conglomerate does not contain the coarsest material and would imply that detritus at the base of the conglomerate was not the most proximal to the source. Equivalent coarser grained basal conglomerates would be anticipated further east in the direction of the palaeosource.

If the average value of maximum clast size in a given vertical section is taken to represent an equilibrium reached in the system, in other words if base level changes in the basin remained constant relative to source block elevation then this is the clast size that would be produced. Significant variation away from the "equilibrium mean" probably represents a tectonic or geomorphic change in the system resulting in fining or coarsening upward trends.

Coarsening and fining upward trends shown on Figs. 3-A and 3-B were produced mainly from the variation in maximum clast size away from the equilibrium mean. Significant variation was taken as one sigma from the overall mean vertical maximum clast size. One sigma in section 1 is 4.1 cm bounding 9.2 cm and 17.4 cm and in section 2 one sigma is 3.4 cm bounding 7.8 cm and 14.6 cm. Any change in maximum clast size falling outside the bounding clast size probably represents a significant short-lived change in the fluvial system. Percentage of sandstone correlates well with the inferred trends.

Coarsening and fining upward trends have been used by number of authors (Steel, 1976, Steel, *et al.* 1977; Blair 1987, Heward, 1978) to infer hydrodynamic and/or geomorphic response to varying tectonic changes in the source block or basin of deposition. Section 1 is dominated by the Gm1 facies and the well stratified beds of the Gm2 facies are not present.

Bedding is poorly developed in the section and an accurate analysis of coarsening or fining upwards units described by Steel (1976); Steel, *et al.* (1977) cannot be made.

The trends that are recognized in the two measured sections are based on the above outlined method. Whereas section 1 shows a number of coarsening and fining upward sequences section 2 has only three recognizable sequences. Section 1 has three separate coarsening upward trends each followed by a thicker fining upward trend giving rise to an overall fining upward trend or megasequence. Section 2, in contrast begins with a coarsening upward trend and is dominated by a fining upward trend until the final stages of sedimentation where a coarsening upward trend is present. As noted earlier sorting within the Gm1 facies in section 2 also improves upward through the section but decreases near the top. The fact that the two sections reveal a dissimilar pattern in the vertical sequences could be a function of downfan changes on a large fan or variation on superimposed fans.

Degradation of the fan surface which has its expression in the development of channels and incision on the fan surface is completely absent from the Straiton conglomerates. The implication is that basin subsidence was greater or equal to uplift in the source region throughout much of the deposition of the conglomerate sequence. The coarsening upward trends could represent secondary fan development in the mid-fan region but the consistency of coarse sediment-laden Gm1 facies in the vertical profiles indicates proximal-fan deposits. The coarsening upward trends probably reflect short-lived renewed uplift in the source region. The increased number of coarsening upward trends in Section 1 could simply reflect the closer proximity of this to the drainage basin compared with section 2.

The prominence of the Gm2 facies in the top of the sequence to the west of section 2, (Fig. 3.1.7), indicates that small longitudinal bars became the dominant morphological feature and signify a change in the fluvial system. Any change in the system needs to account for the decreased roundness, increased disk and rod shaped clasts and increased sandstone associated with the conglomeratic units. A simple change in sandstone lithology in the source region where erosion into thinly laminated sandstones could account for the increased discoidal-rod shaped clasts and associated increase in imbrication. Well developed imbrication associated with both a decrease in clast roundness and a coarsening upward trend is also seen near the top of section 2. The Gm2 ridge exposures west of section 2 and the top of section 2 have thus been tentatively correlated. However, stratification and prominence of Gm2 facies is not seen in the more easterly outcrops. The lateral change to Gm2 facies is probably related to a more steady fluid flow developed by the merger of unconfined flow into shallow channels in the downfan direction (Davis, 1938). These deposits are in turn related to downfan changes 1 km toward the west of section 2 where they interfinger with trough cross-stratified sandstones and conglomerates resembling typical braided stream deposits. The downfan changes from

braid-plain to the more distal braid stream deposits occur in less than 2 km and indicate relatively small fan geometries in the final stages of the conglomeratic sequence west of section 1. It is significant that neither the top nor the base of section 1 and section 2 can be stratigraphically correlated and suggest the deposits are not time-equivalents but section 2 can be related to exposures further west, at least in the upper portions of the conglomeratic sequence. In both sections the end stages of sedimentation are marked by a very rapid change to pebbly conglomerates and gradation into the overlying sandstones.

The sandstone sequence at the base of Section 2 has a source direction antithetic to the conglomerate sequence and cannot be a distal equivalent of the conglomerates to the east. The sandstone sequence is interpreted as distal sheetflood deposits possibly from the west margin of a N-S trending basin. Although the sandstones contain sandstone clasts similar to the clasts in the conglomeratic sequence, petrographically the sandstones have considerably higher proportions of acidic volcanics and very little metamorphic detritus compared to interbedded sandstones within the Greywacke Conglomerate. Blair (1987) showed that fluvial and lacustrine environments respond more quickly to basin subsidence and are displaced toward the basin margin and only when the geomorphic threshold (Heward 1978 fig. 2 based on Schumm 1973) is breached do alluvial fan conglomerates enter the basin. Conglomerate units with the same westerly dispersal as the sandstones are not encountered. The westerly margin although active was never a substantial region of highlands during the Upper Silurian-(?) Early Devonian times. The margin may have had uplifted previously deposited easterly derived alluvial fan sediments as well as acidic volcanics.

Fig. 3.1.7 shows the lithostratigraphic logs in the Straiton area. None of the sections except the above sections (1 and 2) were mapped in detail as exposure is very limited. It can be seen that a substantially thick conglomerate has been mapped in sections 3 and 4 and to some extent section 5. Inspection of Fig. 3.1.8 shows that quite coarse conglomerates are found in the middle portions of these sections, along Auchingairn Burn, with maximum clast sizes up to 20.4 cm. Gm1 facies is dominant in the exposures along the burn and Gm2 facies dominant at the top of Section 3 and 4. It follows that the conglomerates in the middle of these sections are proximal deposits and suggest that repeated faulting to the east of the present exposures occurred throughout deposition of the conglomerates.

The contact between the base of the conglomerate and the sandstones in the base of section 2 is extremely sharp where the conglomerates are in direct contact with rippled sandstones and thus probably represents a disconformity. The conglomerate in section 1 which cannot be correlated to the conglomerate in section 2 may have initially been deposited above the sandstone sequence and eroded off before deposition of the conglomerates in the westerly

sections. The basal sandstone is not developed in the easternmost section (section 1) and the varying thicknesses mapped in the area are difficult to interpret. An uneven topography on which the sandstone was deposited could account for the change in thickness but would also require the Ordovician to form highs. Lithologies found in the Ordovician (see sect 2.1) are not found in the Greywacke Conglomerate indicating the Ordovician was eroded flat prior to sandstone deposition.

b.) Palaeoflow variation. Imbrication measurements indicate a very narrow range in the palaeoflow (Fig. 3.1.8), the source region lying at 10° south of East. This is in contrast with studies of individual ancient and modern alluvial fan conglomerates (Bluck, 1965; Bull, 1972) which have radial flow patterns. Nilsen (1982) points out that uplift along the margins can obscure the radial flow pattern where apexes are continually being eroded.

It seems most likely the small variation in palaeoflow is not attributable to deposition on an individual alluvial fan which had freedom of flow movement but could be explained if the flow was confined or incapable of radial flow. Alternatively, the flow pattern could be explained if the most proximal region was removed and only the braidplain was left. However, facies Gm1 resembles proximal sheetflood deposits and facies Gm2 has been interpreted as the mid-fan braidplain deposits. It seems most probable that the flow in the proximal-fan did not have freedom to swing in a radial way and some process controlled the flow pattern in a unidirectional mode.

Confinement of flow in alluvial fans is usually found only in the wadi zone or above the intersection point if the fan surface is channelled. Channelling is not an important feature in the Straiton conglomerates and would suggest that a process other than a geomorphic process was responsible for the funneling of flow. A possibility is the accumulation of very small alluvial fans in a narrow, rapidly subsiding basin. This could explain all the observable features seen in the conglomerates; lack of channelling, low variation in palaeoflow, and, sheetflood dominated facies.

c.) Clast variation. Clast roundness is remarkably uniform throughout the Straiton conglomerates with the exception of the hillside exposures, Gm2 facies, in section 3 (Fig. 3.1.7). The high degree of rounding especially at the base of the conglomerate suggest the sandstone clasts could have had more than one cycle of sedimentation. At the base of the conglomerate in section 2 well rounded quartzite clasts increase in frequency but never to the extent of being a main constituent. This increase of quartzite clasts is only found within 5 m of the base, above this level quartzite clasts are very rare. These clasts being extremely well rounded have obviously had more than one cycle of erosion and deposition and closely resemble the quartzites in the Quartzite Conglomerate. Similar quartzite clasts are not found in the basal portion of Section 2 but are seen at the base of the Greywacke Conglomerate in

the Hagshaw Hills again implying the conglomerates in section 1 cannot be a time-stratigraphic equivalent of conglomerates in section 2.

If the Gm1 facies interpretation is accurate and deposition of the conglomerates was by sheetfloods without major post-depositional modification then it would seem improbable that one depositional event could produce well rounded sandstone clasts. There could be two possible explanations to explain the degree of roundness in the conglomerates; the clasts could have been reworked within the basin of deposition by renewed tectonic activity which raised previously low level conglomerates, alternatively the clasts could be recycled from older conglomerates outside the basin of deposition. It has already been argued that the margin fault moved within the basin and would favour reworking of the conglomerates within the basin.

The lower degree of rounding in the greywacke clasts in the Gm2 facies, the more distal conglomerates, would indicate that these clasts are first cycle and thus preclude the conglomerates from having a parent in older conglomerates. The mechanism of uplifting and reworking previously deposited gravels ceased during the later stages of conglomerate deposition when the Gm2 facies was being laid down.

The composition and grain size of the individual clasts also remains markedly uniform throughout the conglomerate. Fine-medium and medium-coarse grained sandstones forms the largest percentage of clasts at each of the measured points. Chert percentages generally increase in the lower grain sizes whereas very coarse grained sandstones and granules generally increase in the larger grain sizes. Composition diagrams in section 2, (Fig. 3-B), show a wider variation in gravel lithologies than in section 1, (Fig. 3-A), incorporating small amounts of vein quartz, cherty mudstones, and very fine to silt sized sandstones. The increase of vein quartz and to a lesser extent cherty mudstones could be easily explained by downvalley increase in the more resistant material relative to the major bedload but the introduction of silt to very fine-grained sandstone clasts, which are generally thinly laminated and thus easier split, cannot and would require a change in the source rock between the two sections, again indicating a difference between the two sections.

3.2 Hagshaw Hills.

The Greywacke Conglomerate exposures in the Hagshaw Hills inlier are confined to the bottom of the burn channels with rare 2-dimensional exposure along the margins of the more incised portions of the burn. The underlying fluvial sandstones, thought to be of Llandovery age, pass conformably up into the Greywacke Conglomerate. The conglomerates closely resemble the Greywacke Conglomerate in the Straiton area.

3.2.1 Facies.

Three vertical sections, Figs. 3-(C-E) have been logged in the Hagshaw Hills area following the methods described in sect. 3.1.3. The location of the sections are given in Fig. 3.2.1.

The Greywacke Conglomerate is dominated by the Gm1 facies; poorly-sorted, clast-supported conglomerates with a matrix of coarse-very coarse sand. The Gm1 facies has properties similar to the Gm1 facies in the Straiton area and were probably deposited by sediment-laden sheetflood deposits in the proximal regions of alluvial fans. Bth vs Mcs shows a positive correlation (Fig. 3.2.2), again indicating rapid deposition of sediment charged fluid flows.

Occasional thin discrete sandstone units occur throughout the Gm1 facies but increase in frequency near the top of the conglomerate and in major fining-upward sequences. The sandstones and conglomerates repeat on average every 50-55 cm, conglomerates average 40 cm and sandstones 10-15 cm in thickness. The conglomerate thickness resembles that recorded in the Straiton Gm2 facies but there are differences between the two. The Gm2 facies has very little sandstone and imbrication is widespread whereas in the sandstone-conglomerate package, type 2 facies of McGiven (1967), imbrication is rare. The conglomerates show a positive correlation between bth and mcs where many of the data points in Fig. 3.2.2 are taken from the sandstone-conglomerate package. The correlation coefficient, $r=0.76$, is even higher in the Hagshaw Hills than in either the Gm1 or Gm2 Straiton conglomerates. Although these conglomeratic units occur in fining-upward sequences they do not show a significant difference in clast size from the massive structureless conglomerates. It would therefore seem that the conglomerates are not unit bars in proximal braid-plains but instead represent, Gm1 facies, sheetflood deposits from a diminishing hinterland or a subsequent shift towards more distal regions of proximal fan deposits.

3.2.2 Vertical and lateral variation.

a). Facies and maximum clast size variation. Section 1, (Fig. 3-C), has a consistently coarser grain-size and lower percentage of sandstone than either section 3 or section 5. The section is dominated by Gm1 facies conglomerates and represents the most proximal section studied in the Hagshaw Hills. The section is also dominated by fining-upward trends with two short-lived coarsening-upward trends. The fining-upward trends may represent renewed fault activity in an even more proximal area leading to coarser material not significantly different from the "equilibrium clast size" entering the basin of deposition. The coarsening-upward trends with a significant increase in clast size can either indicate coarse channel deposits incised into the fan surface or renewed fault activity within the basin of deposition.

Erosional features are not seen in section 1 but are seen in section 3 where very coarse conglomerates scour underlying sandstones. This suggests that the coarsening-upward sequences are channel deposits on a degrading fan surface. Thus, basin subsidence did not always equal or exceed uplift in the source region, however there are very few coarsening-upward trends with the majority of sediments probably deposited in a rapidly subsiding basin.

Section 3, Fig. 3-D, and section 5, Fig. 3-E, both have repeating sandstone-conglomerate packages at lower levels in the sections than seen in section 1. The first occurrence of these packages is close to the base in section 5, near the middle in section 3, and only near the top in section 1. This along with the percent of sandstone and maximum clast size distribution, Fig. 3-(C-E) and Fig. 3.2.3, indicates that section 5 contains the most distal fan deposits and section 3 contains deposits somewhere between section 5 and the more proximal section 1. This relationship is maintained throughout deposition of the Greywacke Conglomerate. The distances between the proximal and more distal regions is approximately 1 Km and suggests the fan bodies were relatively small.

Again, where the final stages of sedimentation can be seen in the conglomerates there is a rapid change from coarse to pebbly conglomerates.

b). **Palaeoflow variation.** Imbrication is poorly developed in the conglomerates and is probably a function of both rapid deposition from sediment-laden fluid flows and high degree of roundness of the clasts. The imbrication does however suggest a source to the east, (Fig. 3.2.4), in the most proximal sections. The change to a more southerly direction in section 5, the more distal fan deposits, could simply reflect the angle from the apex of an adjacent small fan. A shift to north directed palaeocurrents near the top of the conglomerate in section 1 and west-southwest directed palaeocurrents near the top of section 5 is difficult to explain. A shift, by transcurrent motion, of the basin margin relative to the source block could explain one of the changes in palaeocurrent direction but not both. A separation of one fan into a number of small fans could explain the variation but would indicate large-scale vertical movement between the source block and the basin, whereas the sediments near the top of the sections are fine-grained conglomerates deposited during the final stages of erosion of the source block.

c). **Clast composition and roundness variation.** The composition of the conglomerate does not show any major variation upward through the Greywacke Conglomerate. Sandstones are the major constituent with small percentages of chert, cherty mudstone, and metamorphosed sandstones. Metamorphic quartzites are found only near the base of the conglomerate, similar to that observed in the Straiton conglomerates. The grainsize of the

sandstone clasts does not differ between the sections or from the Straiton conglomerates, the majority being fine-coarse grained sandstones. In contrast to the Straiton conglomerates the Hagshaw Hills conglomerates have higher percentages of chert and cherty mudstone and lower percentages of very coarse-granule sized sandstones.

The degree of roundness of the clasts is high throughout the vertical profiles. The clasts are typically rounded to well rounded and again argue for continual reworking of the clasts within the basin of deposition.

3.3 Tinto-Carmichael.

The Tinto and Carmichael sequences are both conformable on the underlying Silurian fluvial sandstones. Exposures are very poor in both regions and generally confined to small isolated outcrops and disused quarries. The Tinto Felsite, a large rhyo-dacitic intrusion, cuts the Greywacke Conglomerate in the Tinto area and similar sill-like intrusions are found in the Carmichael area but occur mainly in the sandstones overlying the Greywacke Conglomerate. As noted earlier the Tinto Felsite has been dated at 412 ± 1.5 Ma.

3.3.1. Facies.

The facies and facies associations closely resemble those seen in the Hagshaw Hills sections. The conglomerates are coarse structureless conglomerates with occasional thin sandstone tops equivalent to the Gm1 facies. Bedding contacts within the Gm1 facies are poorly defined but where discernible, the Tinto conglomerates, show a positive correlation between Mcs and Bth, (Fig. 3.3.1). The correlation coefficient, $r=0.84$, is higher than either the Straiton or the Hagshaw Hills conglomerates and suggests the Tinto conglomerates were deposited in very close proximity to the source block. In the Carmichael region a sandstone-conglomerate association occurs. The contacts between the sandstones and conglomerates are sharp and each unit is characterized by plane laminated sandstone tops of probable upper flow regime origin.

3.3.2 Vertical and lateral variation.

a). **Facies and maximum clast size variation.** In the Tinto region the lateral distribution of facies and maximum clast size is difficult to correlate due to the random nature of the outcrop localities. Figs. 3.3.2 and 3.3.3 shows the location of the exposures and associated facies in the Tinto region. Exposures of very coarse to coarse-grained massive sandstones with occasional cobbles and pebbles of greywacke clasts increase in frequency towards the west. The sandstones occur at vertical heights where coarse Gm1 facies conglomerates were accumulating towards the east and the entire Greywacke Conglomerate thins towards the east (based on mapped outcrop limits). Cross-bedding is either absent or very difficult to define in the sandstones and it is therefore not known if the sandstones truly represent a downfan change to sheetflood sandstones.

Maximum clast size throughout the Tinto Greywacke Conglomerate, (Fig. 3.3.4), is low compared to conglomerates in the Straiton and Hagshaw Hills and may indicate a more active reworking and breaking down of grain size in the conglomerates but however it may also be due to limited exposure. Vertical changes in maximum clast size is best seen in section 4 where a decrease in maximum clast size takes place only in the final stages of deposition of the conglomerate.

In the Carmichael region the "Greywacke Conglomerate" is exposed in isolated outcrops at approximately the same height above the base of the conglomerate along a 0.7 km ridge exposure. The frequency of sandstone increases toward the west, (Fig. 3.3.5) and is accompanied by a slight decrease in maximum clast size in the same direction. The lateral change in facies from coarse conglomerates in the east to a repetition of Gm1 facies and high energy fluvial sandstones toward the west clearly indicates downfan changes. The change to fluvial sandstones in both the Tinto and Carmichael regions is very rapid and argues for the vertical stacking of small fans similar to both the Hagshaw Hills and Straiton conglomerates.

b). **Palaeoflow variation.** Palaeoflow measurements taken from poorly imbricated conglomerates in both the Tinto and Carmichael areas show a dispersal towards the west-southwest (Fig. 3.3.6). Although, this is in contrast to previous work by McGiven (1967) who suggested a dispersal toward the northwest for the conglomerates the lateral facies changes, particularly in the Carmichael region supports the conclusions from this study for an east-northeast source.

c). **Clast composition and roundness variation.** Clast composition in the Tinto conglomerates does not change significantly within the conglomerate with a predominance of fine-coarse sandstone clasts throughout the conglomerate (Fig. 3.3.7a). However, a decrease in roundness is associated with a substantial increase in angular felsite clasts in the Tinto conglomerate. The clasts closely resemble the Tinto Felsite and occur in conglomerates below the main Tinto Felsite. This indicates that intrusion of the felsites occurred at very high crustal levels and were being eroded at the same time as deposition of the conglomerate. This places the age of the Greywacke Conglomerate at approximately the same age as the Felsite, that is latest Silurian-(?) Early Devonian. The felsite clasts do not occur in the Hagshaw Hills and supports the idea that the fans were not of large areal extent. Basalt, although rare, chert, and metamorphosed sandstones occur in greater frequency than in either the Hagshaw Hills or Straiton conglomerates. The metamorphosed sandstones are possibly the product of earlier felsite-intruded conglomerates.

The composition of the "Greywacke Conglomerate" in the Carmichael region is very different to that recorded in the remaining areas. The conglomerate has a very high proportion of metaquartzites and acidic volcanics and includes acidic plutonics, (Fig. 3.3.7b). The conglomerate closely resembles the Quartzite Conglomerate and either indicates that the conglomerate has been mapped in error or that a source block which gave rise to the Quartzite Conglomerate was still being eroded during the latest Silurian. In either case the palaeoflow direction and facies variation suggest a source to the east-northeast. This has implications for the Quartzite Conglomerate. McGiven (*ibid*) suggested a southerly source for the Quartzite Conglomerate and either his conclusions are wrong or the source block for the Quartzite Conglomerate during Late Silurian times was shifted towards the northeast during latest Silurian times.

3.4 North Esk.

The North Esk Greywacke Conglomerate unconformably overlies the vertical Silurian sediments in the northeastern southern Midland Valley. Felsite intrusions cut the Greywacke Conglomerate in the far northeastern exposures in the North Esk. Exposures are again very poor and confined to the bottom and margins of burns.

3.4.1. Facies.

The majority of the conglomerate is a coarse Gm1 facies conglomerate. Bedding contacts within the Gm1 facies are very poorly developed. A repetition of sandstone and conglomerate similar to that seen in the Hagshaw Hills does occur but in contrast to the Hagshaw Hills the sandstones units occur with much less frequency and are separated by thicker conglomerate units.

3.4.2. Vertical and lateral variation.

a). **Facies and maximum clast size variation.** Two vertical sections have been logged and are shown in Figs. 3- (F-G), localities given in Fig. 3.4.1. Section 2, (Fig. 3-G) shows a sequence of very coarse conglomerates throughout much of the lower half of the section. Although section 1, (Fig. 3-F), has limited exposure the conglomerates are overall much finer-grained and indicate more distal conglomerates compared to section 2. Very coarse conglomerates northeast of section 2 are exposed and have the highest maximum clast sizes recorded throughout the entire Greywacke Conglomerate, (Fig. 3.4.2).

Near the top of the conglomerate in section 2 the burn marks the contact between sandstones to the east and conglomerates to the west. Although the contact is not seen the presence of a faulted contact is a distinct possibility where an abrupt change from coarse conglomerates to sandstones across bedding is seen. The sandstones are extensively jointed and

disrupted by minor fractures and again argues for a faulted contact. A minor fault is mapped near the middle of section 2 where coarse conglomerates are again adjacent to sandstones. It is therefore impossible to draw accurate correlations between the two sections above these faults.

The upper and basal contacts of the thick sandstones and the conglomerates are seen in section 1 where they are sharp and non-erosional. The sandstones are typically flaggy and mica-rich with rare small scale cross-bedding.

b). **Palaeoflow variation.** Rare imbricated clasts within the Gm1 facies conglomerates show a bimodal flow towards the west-southwest and west-northwest, (Fig. 3.4.3), indicating a source toward the east. Palaeoflow measurements from sandstones in section 1 and 2 and in the far northeastern exposures all show a flow direction towards the south. It may be that these sandstones are axially derived fluvial sandstones which encroach upon the fan surfaces during periods of little tectonic activity.

c). **Clast composition and roundness variation.** The composition of the conglomerates is similar to the conglomerates in the Hagshaw Hills, Tinto, and Straiton areas. Sandstones, particularly fine-coarse grained, account for the majority of the clasts. There is an increase in fine-grained igneous rocks in the 0-5 cm range compared with conglomerates from the remaining areas. The igneous rocks include both felsitic and doleritic clasts. The basic igneous clasts are easily confused with basic fine-grained sandstones and difficulty in distinguishing between the two may have introduced some error in modal abundances. Large clasts of angular felsite are found in the northeastern conglomerate exposures close to felsite intrusions, a situation similar to the Tinto conglomerates where similar ages for intrusion of felsites and deposition of the Greywacke Conglomerate was suggested. Baked sandstone clasts are also frequently encountered in the North Esk conglomerates, again probably associated with the felsite intrusions.

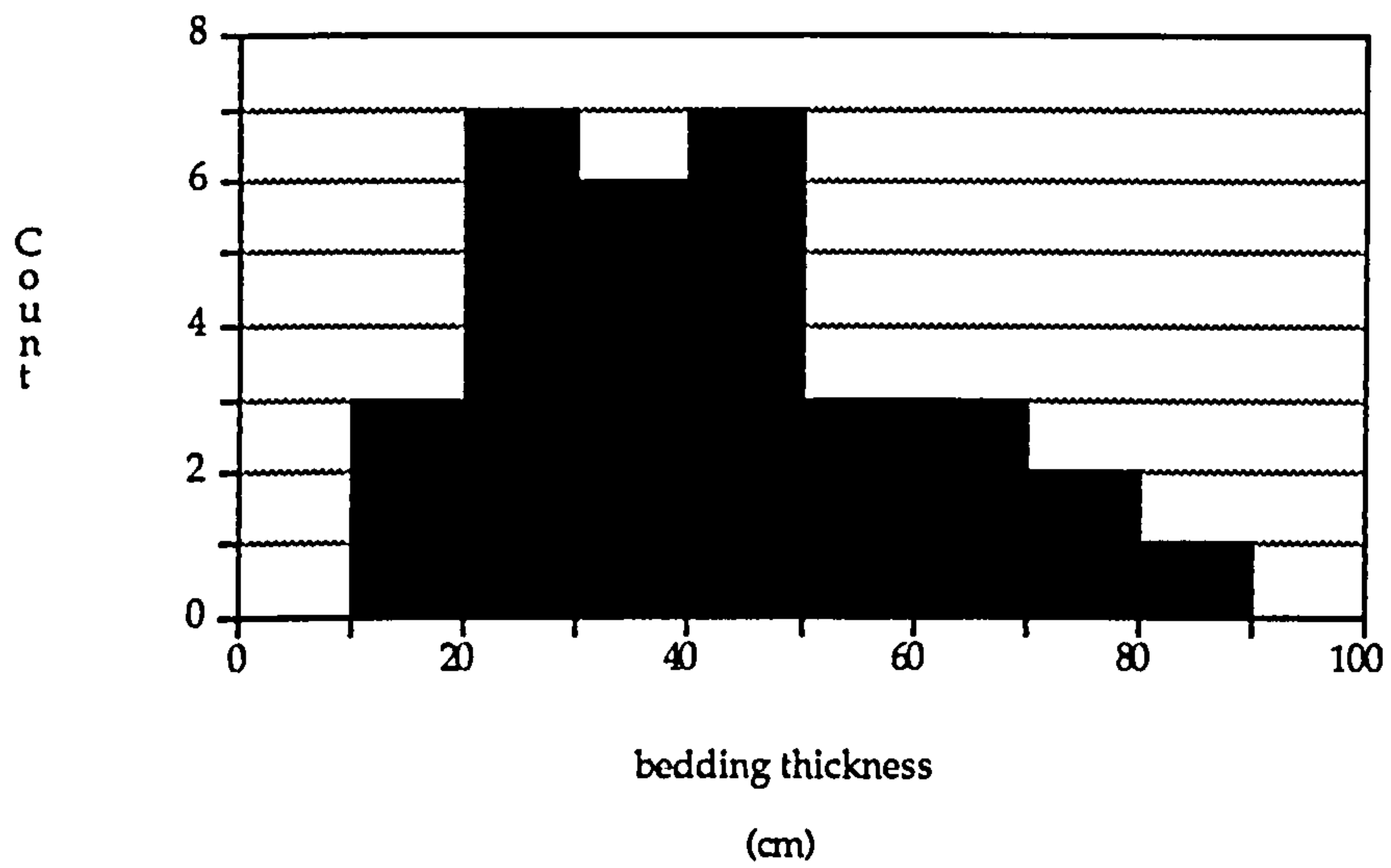
Roundness values are generally high throughout the conglomerate. A decrease in the overall roundness at the base of the conglomerate in section 1 is attributable to the increase in angular felsite clasts. The sandstone clasts are consistently rounded to well rounded.

3.5. Conclusions.

1). Two distinct conglomerate facies are recognized: i). the Gm1 facies and ii). the Gm2 facies. The Gm1 facies is interpreted as high energy sediment-laden fluid flow deposits in proximal fan regions. The Gm2 facies is interpreted as small longitudinal or diagonal unit bars in proximal to mid-fan braid-plains.

- 2). The lateral geometry of the conglomerate and associated facies indicates a vertical stacking of small alluvial fans.
- 3). The majority of the Greywacke Conglomerate in the Midland Valley is dominated by the Gm1 facies and suggest subsidence kept pace or exceeded uplift throughout much of the conglomerate deposition.
- 4). Roundness values indicate uplift and continual reworking of previous low-level conglomerates. A change to fine-grained and braid-plain conglomerates seen in the final stages of deposition suggest a very rapid change to a much subdued, both tectonically and vertically, source block.
- 5). The mean palaeoflow direction for each area, (Fig. 3.5.1), shows the source region for the conglomerates lay to the east with some dispersal from both the east-southeast and north-northeast. This is contrary to previous investigations which proposed a source to the south-southeast for the Greywacke Conglomerate. High-energy distal sheetflood sandstones dispersed from the west-southwest are seen in the Straiton area.
- 6). Although, the conglomerates were dispersed from an easterly source the size of the clasts is remarkably uniform with only a very slight increase in maximum clast size in the most easterly exposures.
- 7). The Greywacke Conglomerate, at least in the Tinto and possibly the North Esk regions, can be accurately dated at the time of the Tinto Felsite intrusion. The Tinto Felsite is currently thought to be 411 ± 1.9 Ma.

Gm1 Facies

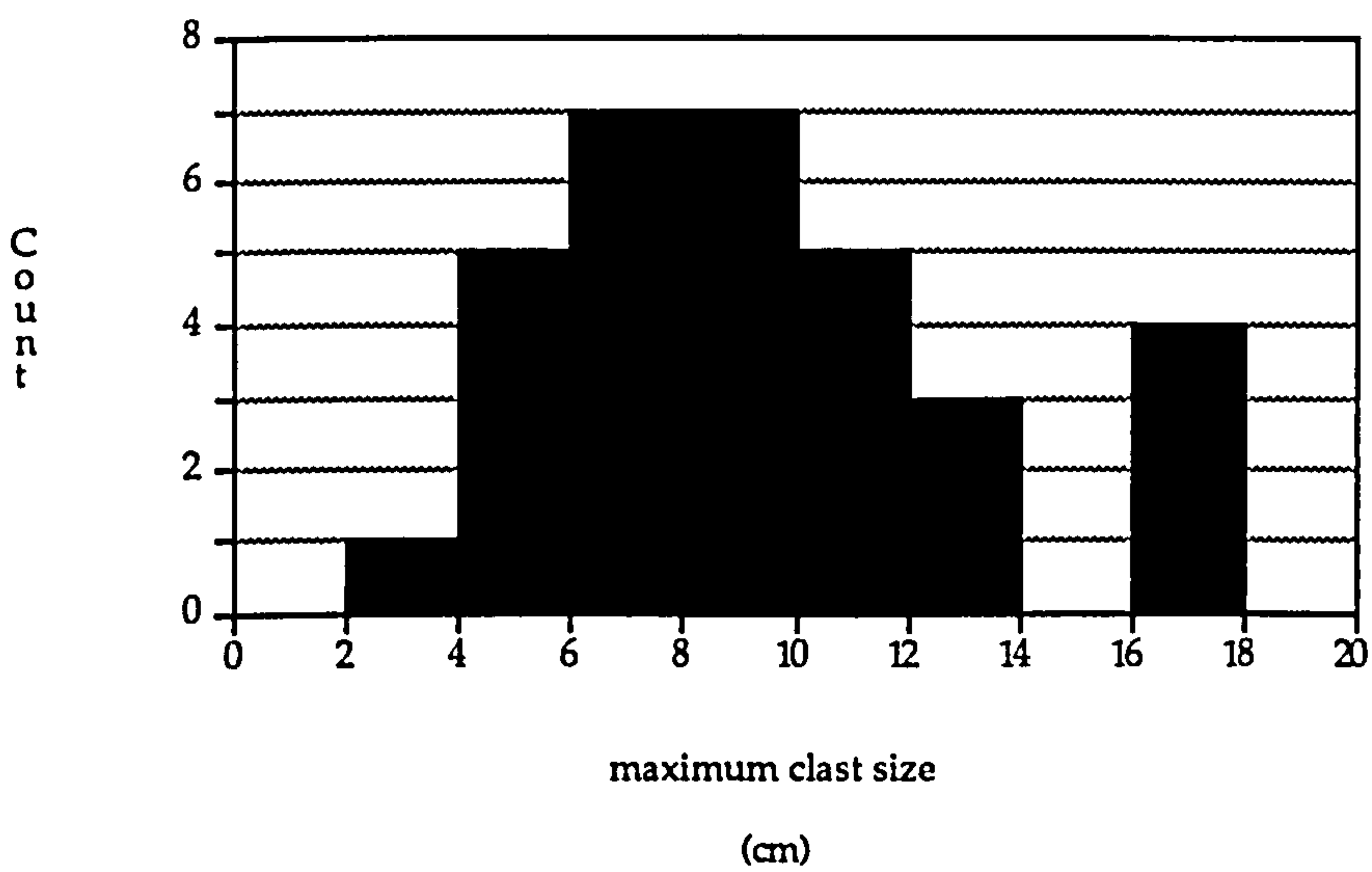


a).

mean = 40.6

1 sigma = 17.9

skewness = 0.7



b).

mean = 9.3

1 sigma = 3.8

skewness = 0.6

Fig. 3.1.1 Bth and MCS histograms from Gm1 facies in Straiton Greywacke Conglomerate

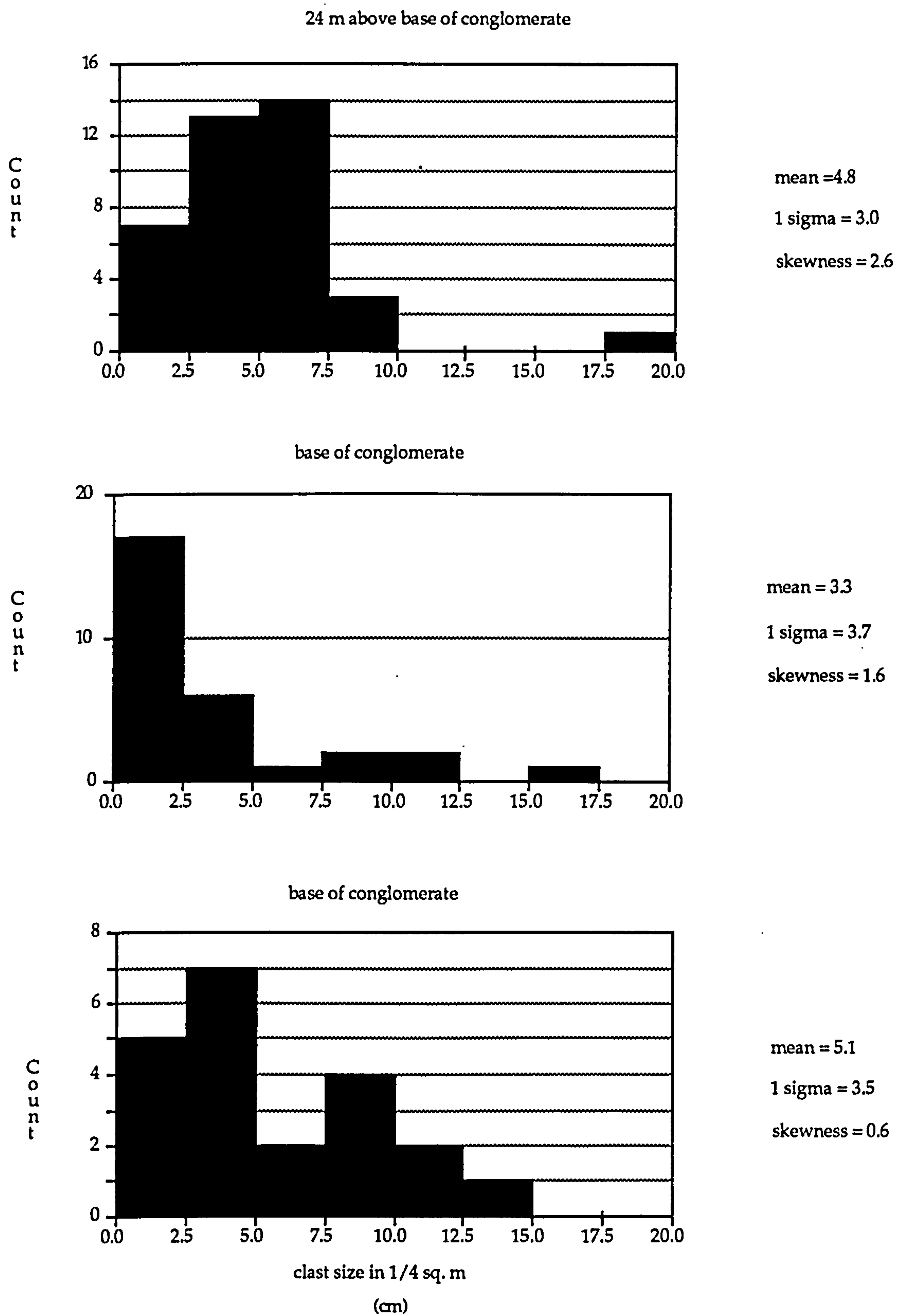


Fig. 3.1.2 Sorting histograms from Gm1 facies, Straiton section 2

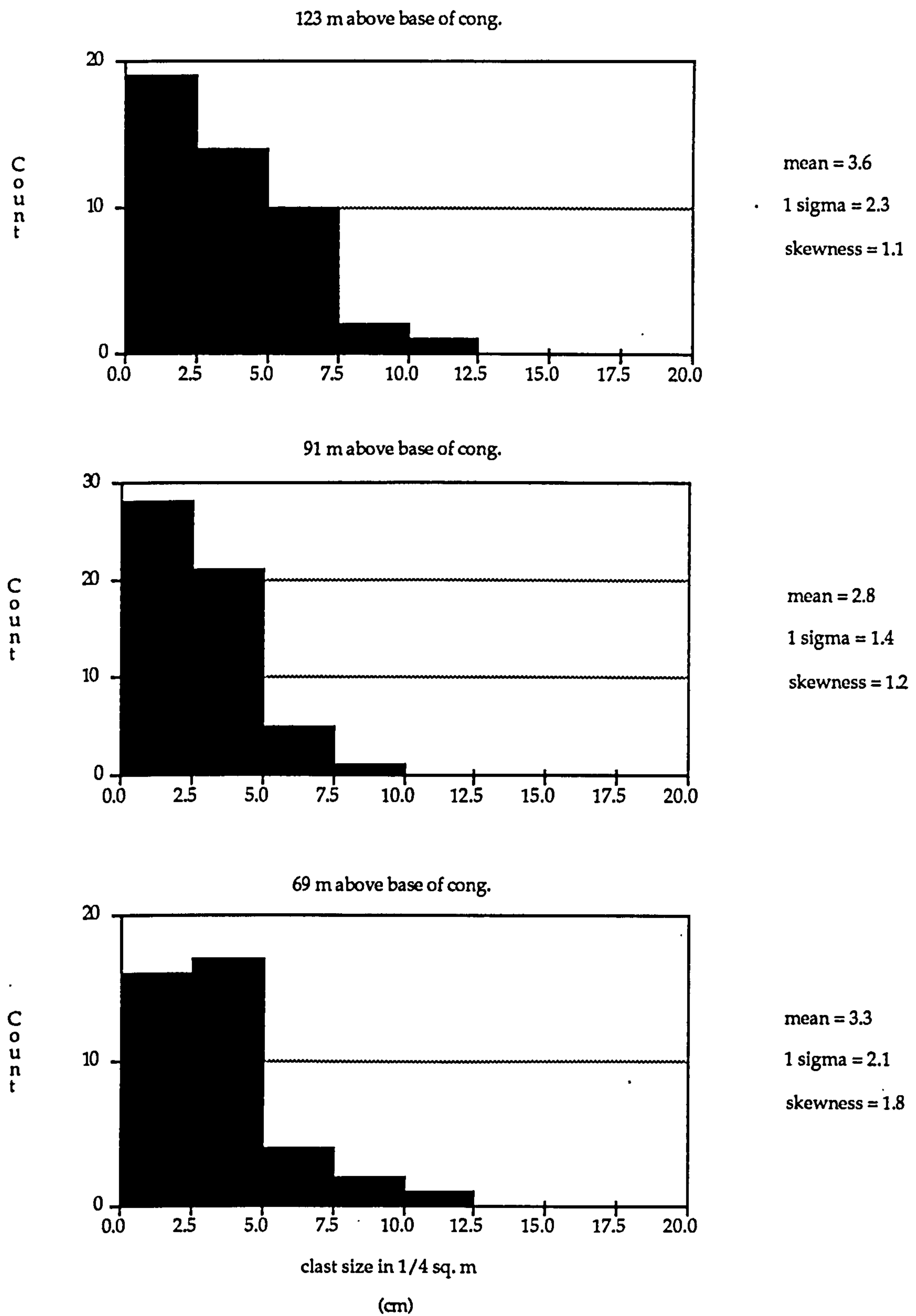
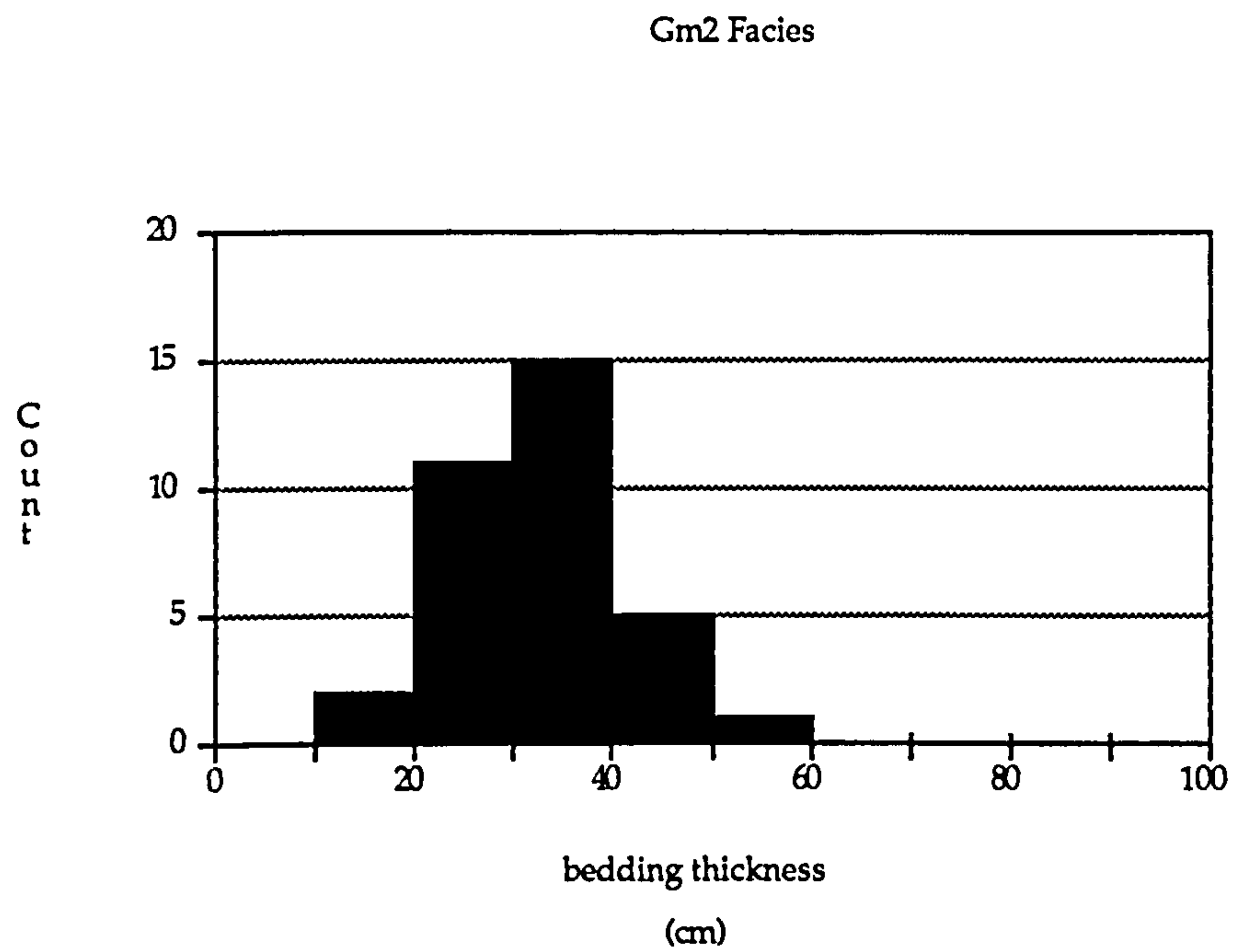
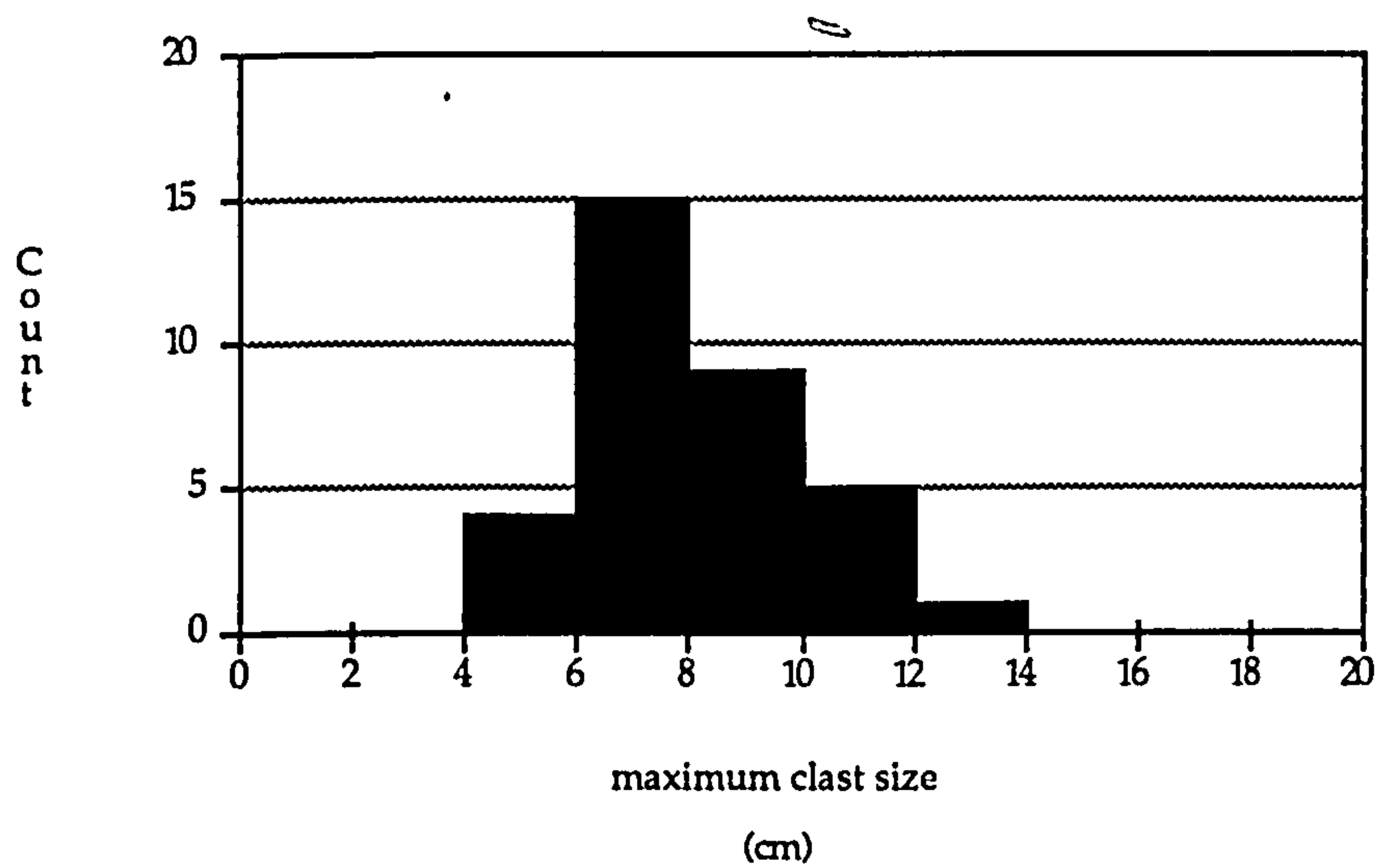


Fig. 3.1.2 (cont.)



a).
 mean = 31.2
 1 sigma = 8.6
 skewness = 0.4



b).
 mean = 8.0
 1 sigma = 1.9
 skewness = 1.0

Fig. 3.1.3 Bth and MCS histograms from Gm2 facies in Straiton Greywacke Conglomerate

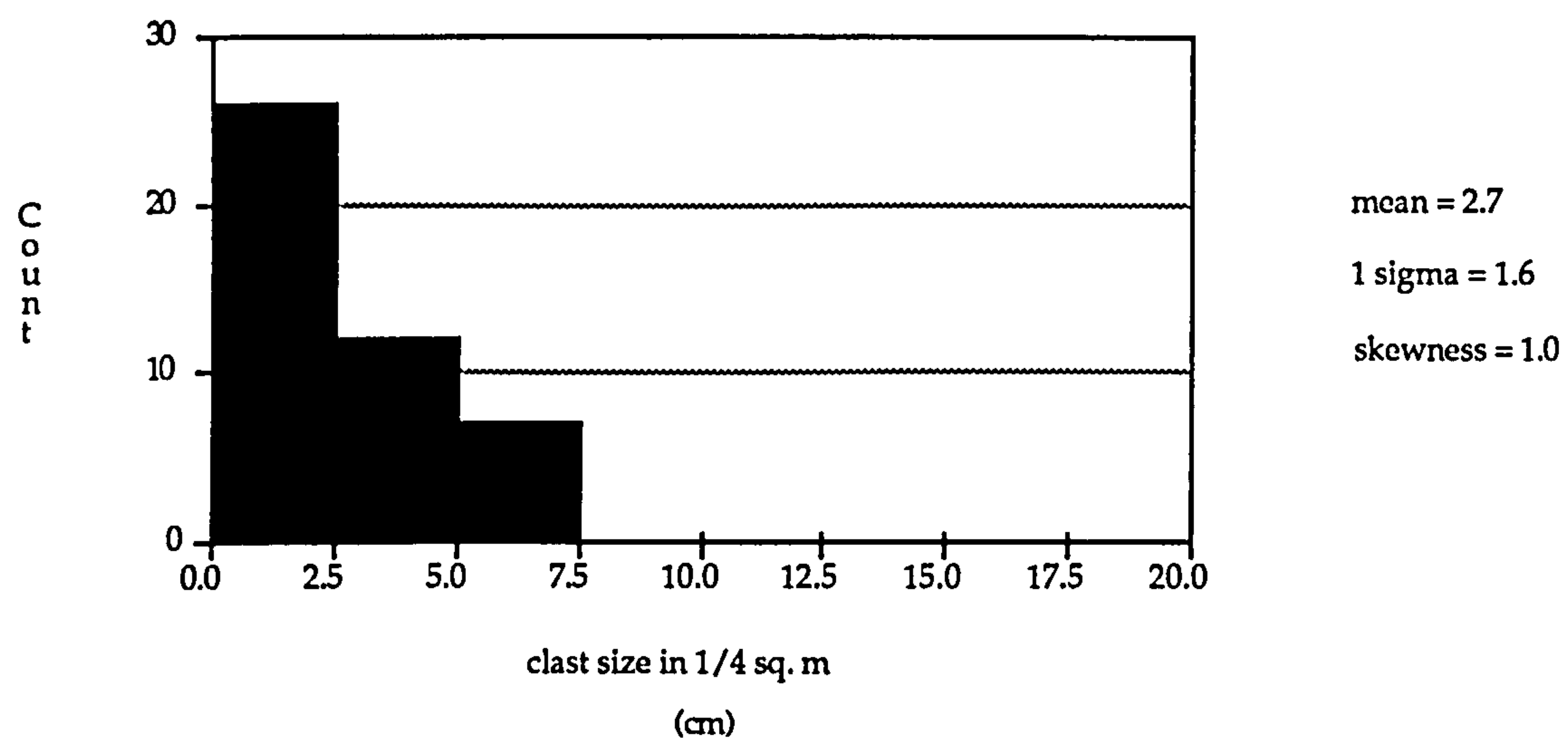
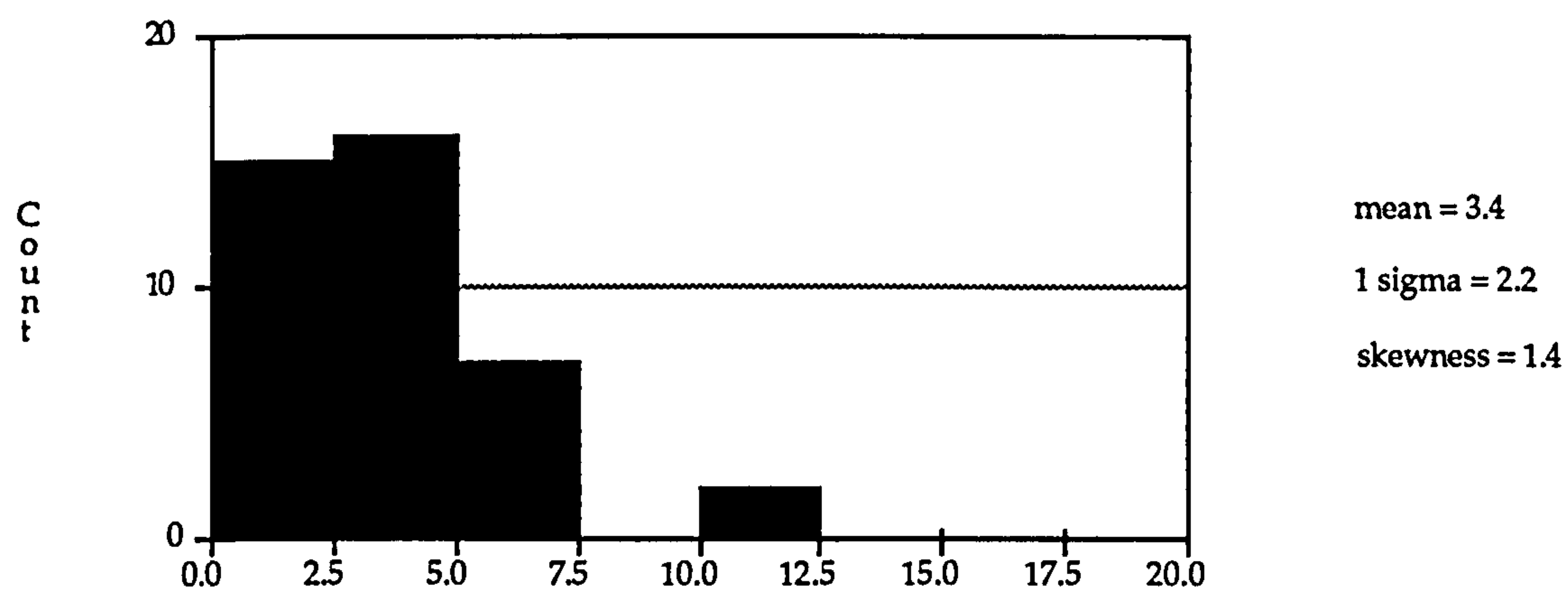
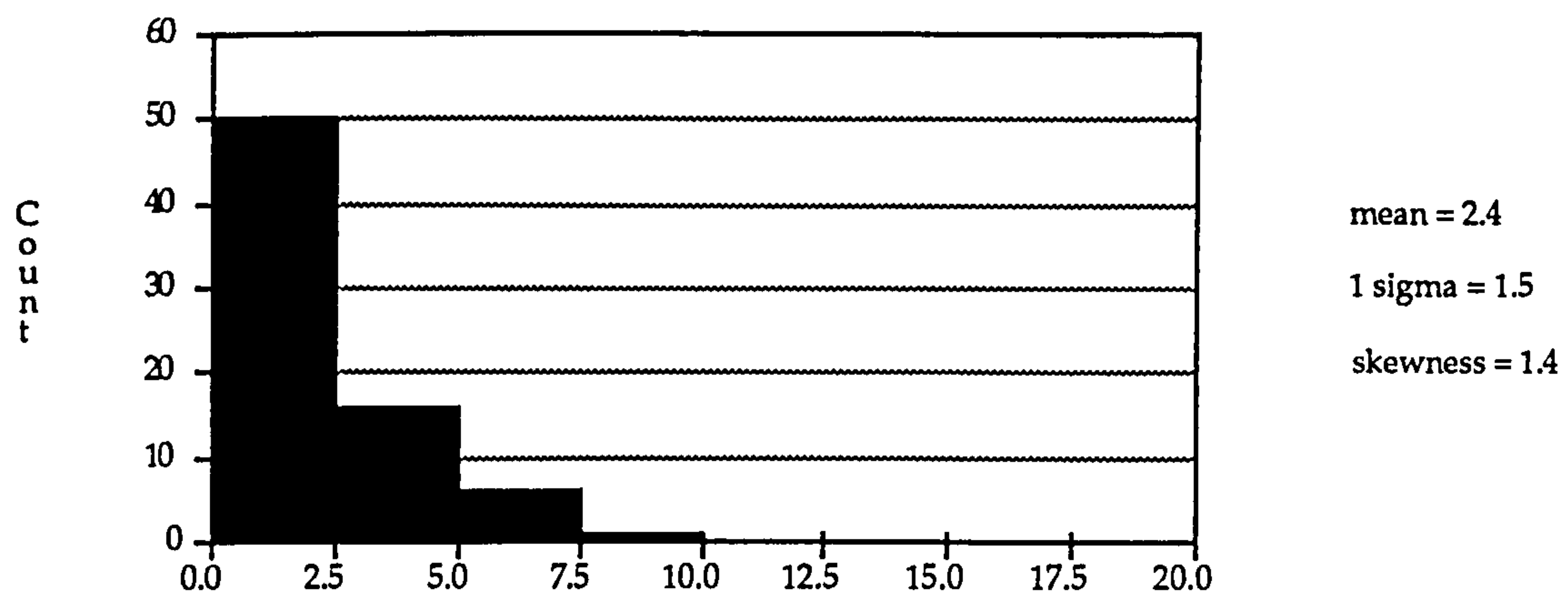


Fig. 3.1.4 Sorting histograms from Gm2 facies, Straiton ridge exposures below Doubty Hill, located top of conglomerate section 3.

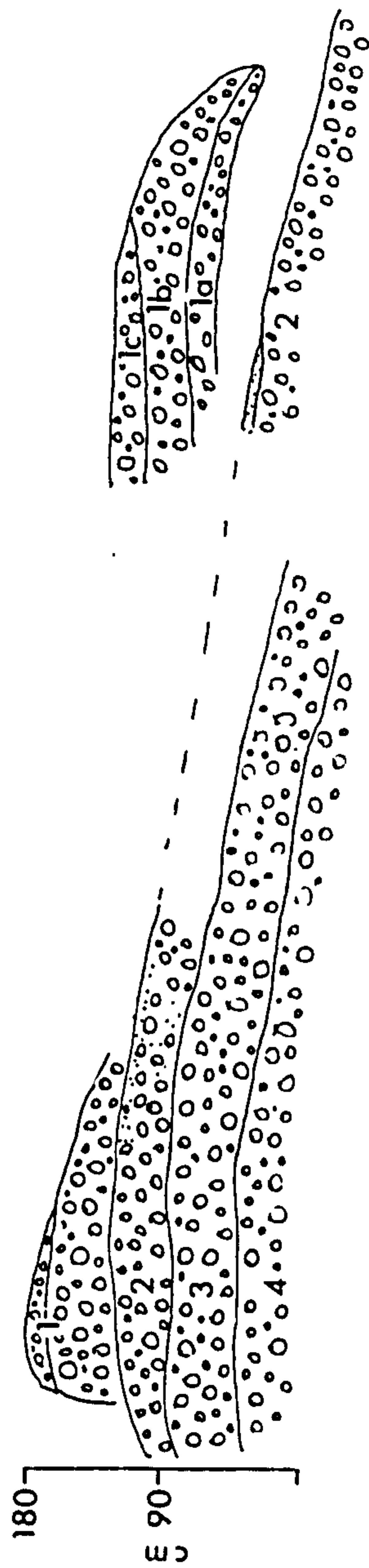
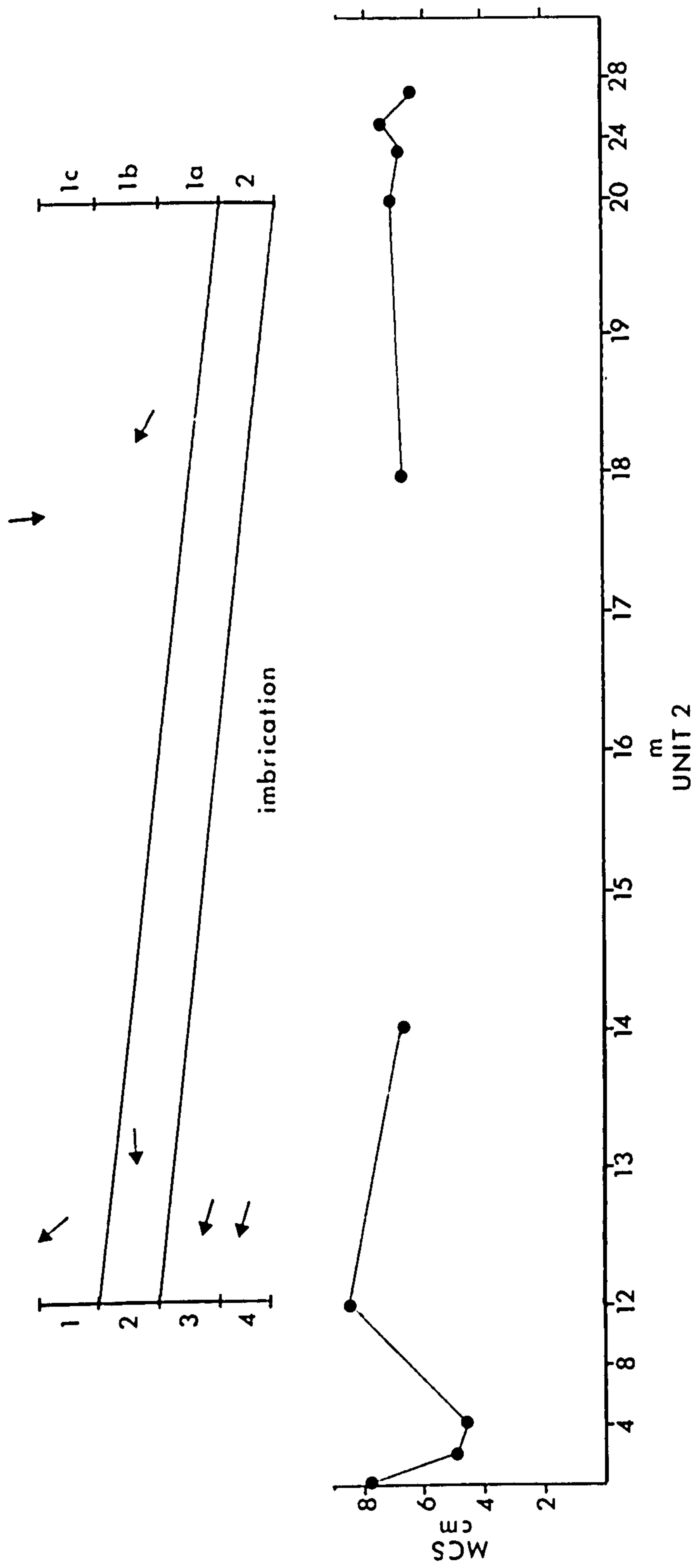
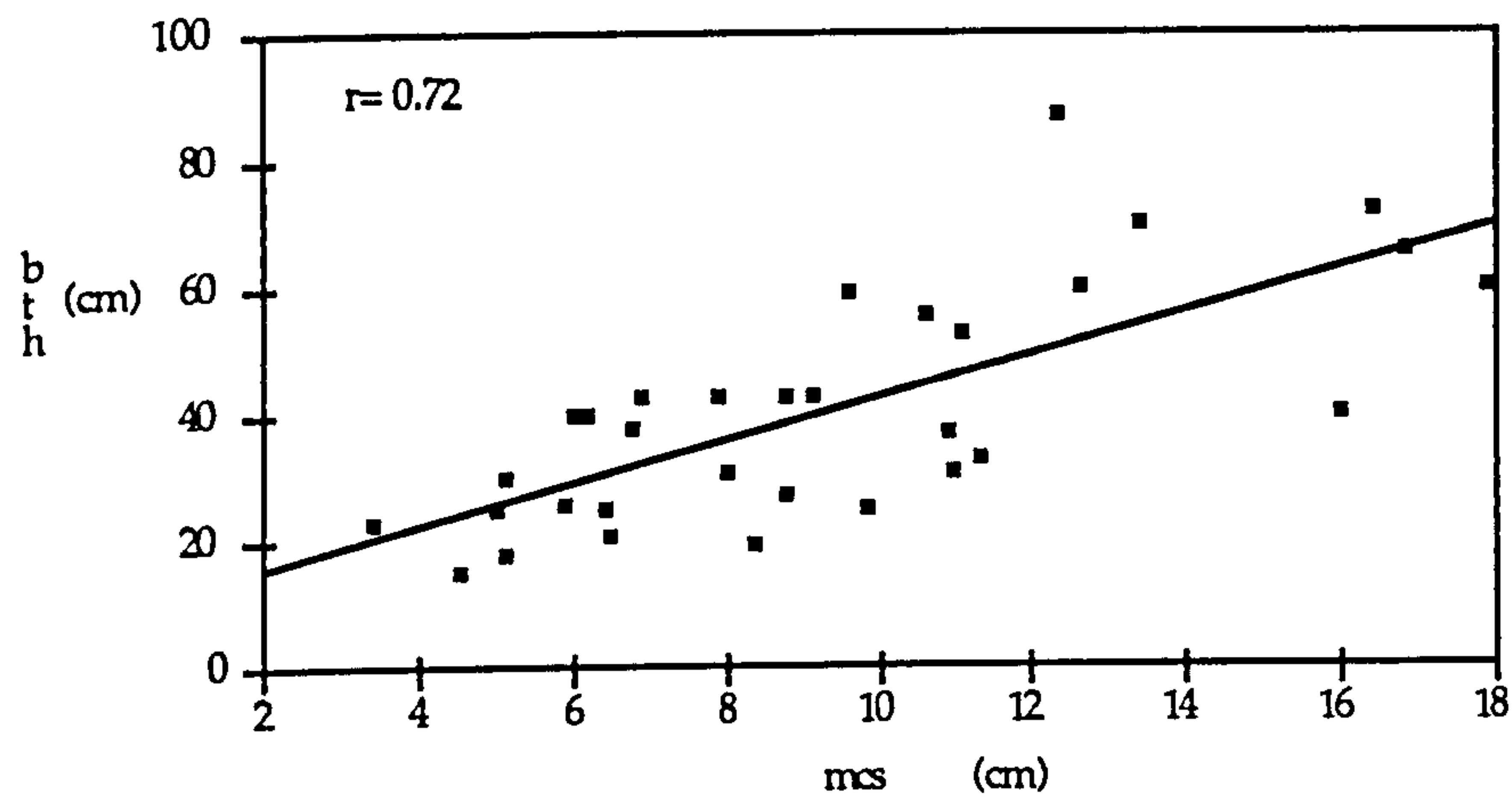
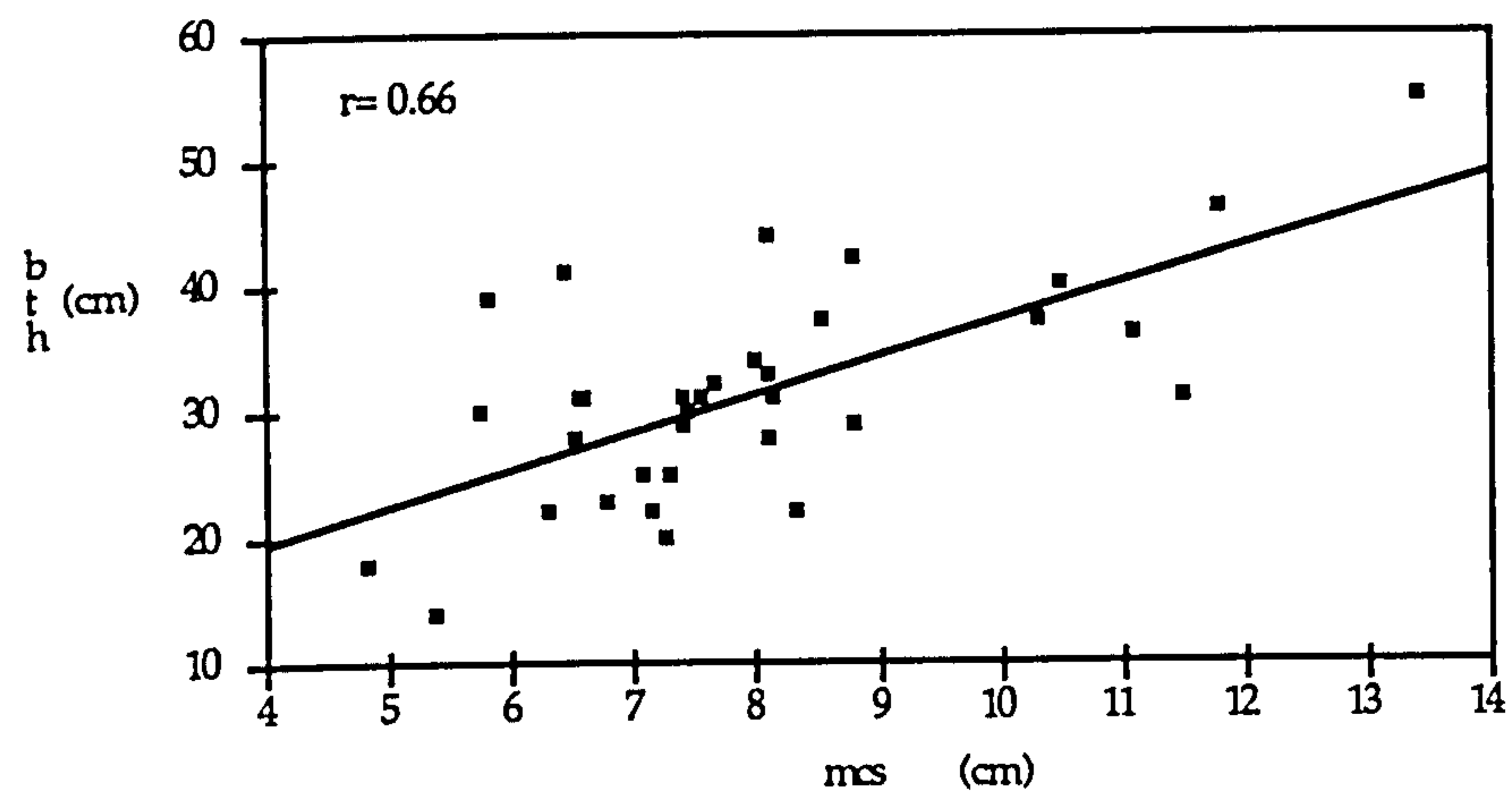


fig. 3.1.5

showing large variation in palaeoflow in Gm2 facies Unit 1



a). Gm1



b). Gm2

Fig. 3.1.6 MCS vs Bth linear regression, Stration Gm1 & Gm2 facies

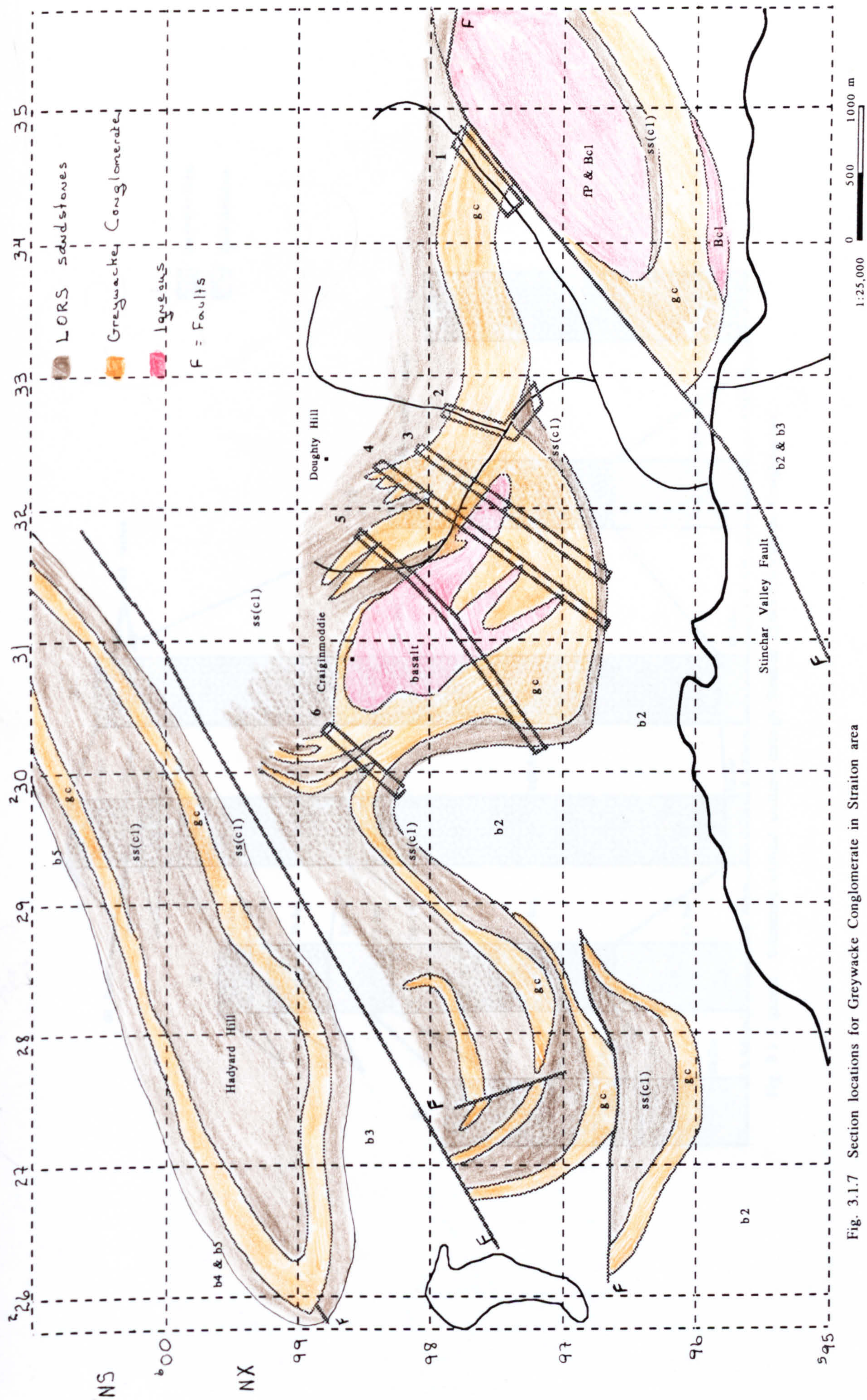


Fig. 3.1.7 Section locations for Greywacke Conglomerate in Straiton area

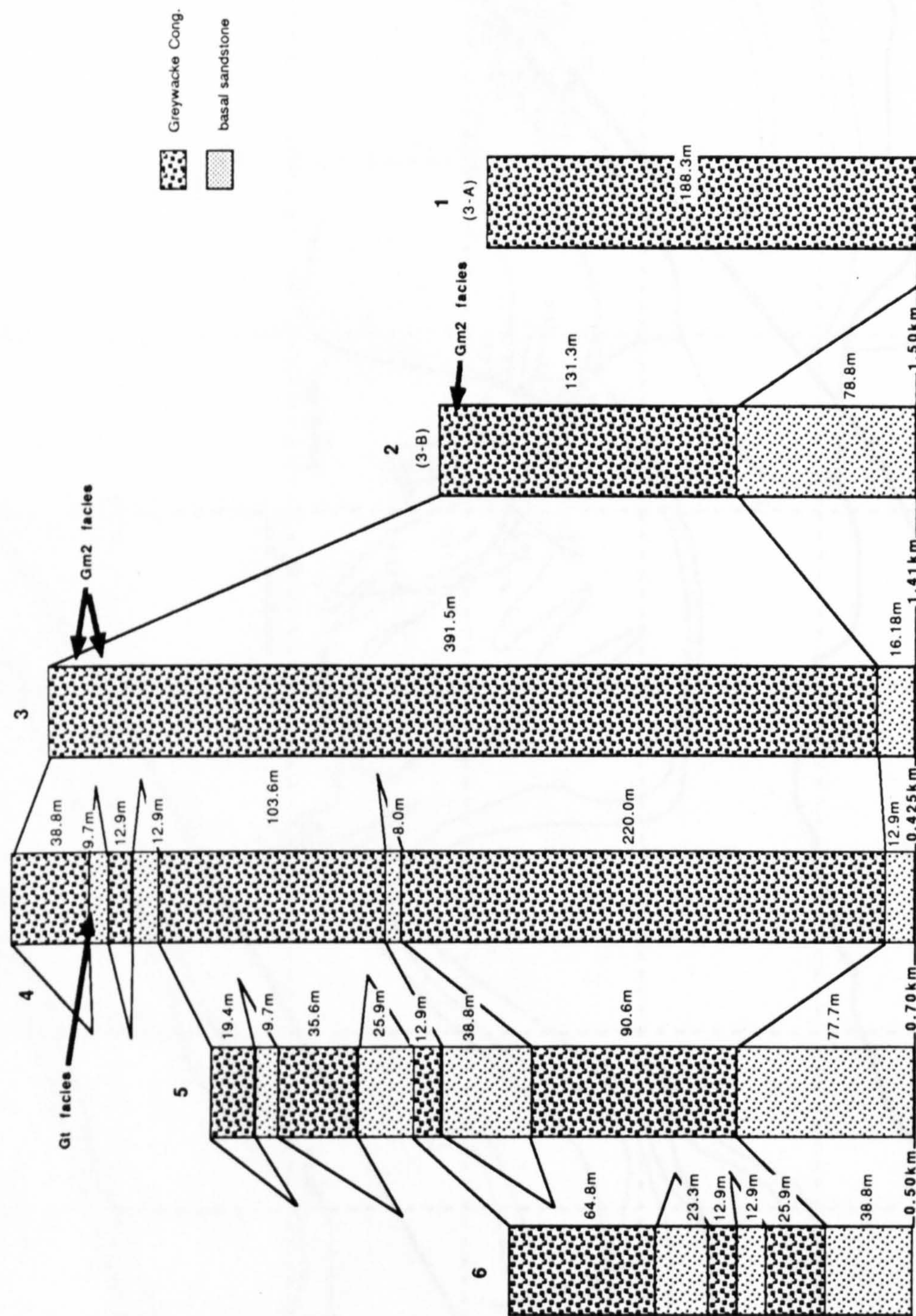


Fig. 3.1.7 (cont.) Schematic vertical sections through Straiton LORS Greywacke Conglomerate

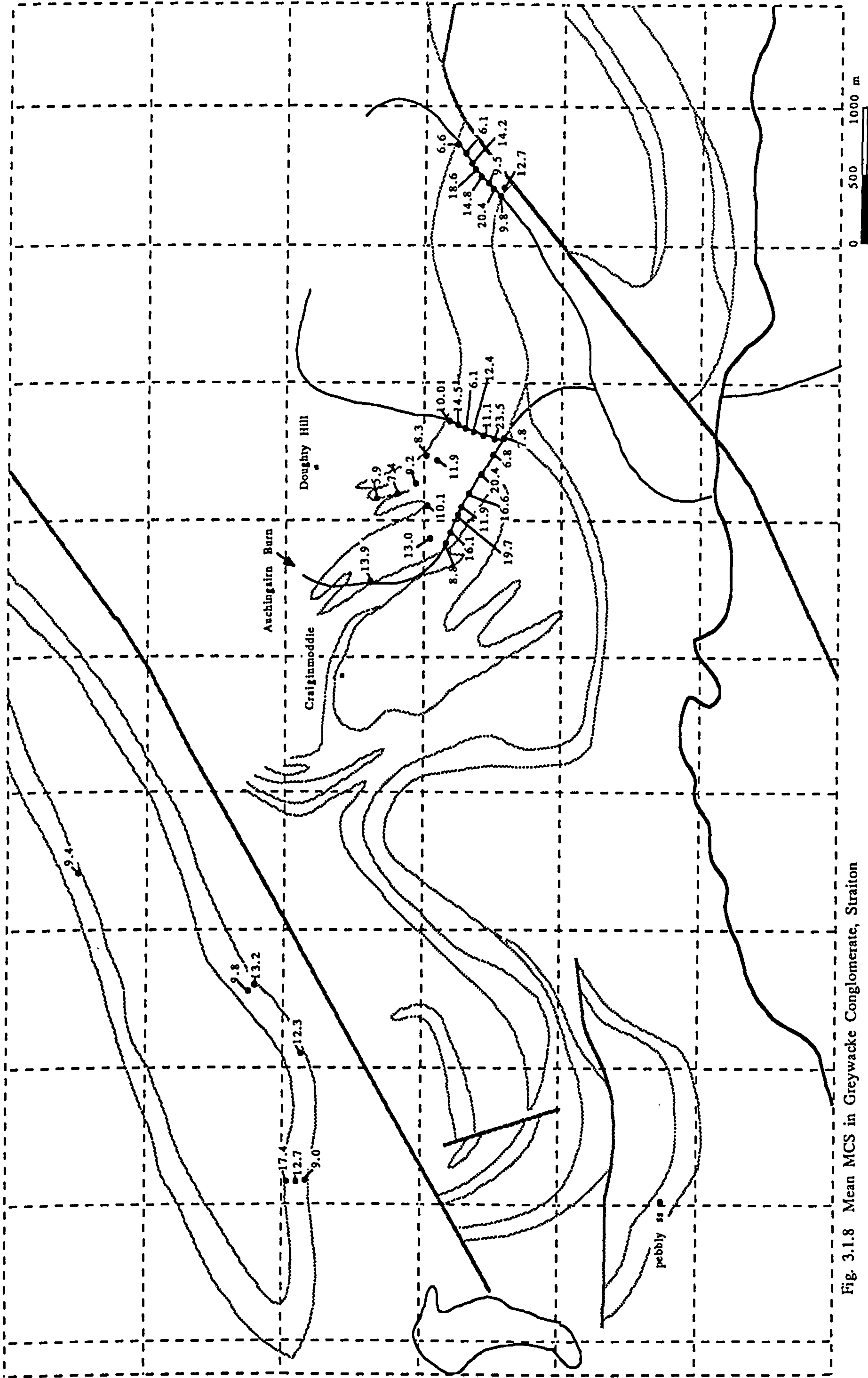


Fig. 3.1.8 Mean MCS in Greywacke Conglomerate, Straiton



Fig. 3.1.9 Palaeoflow vectors for Greywacke Conglomerate, Straiton

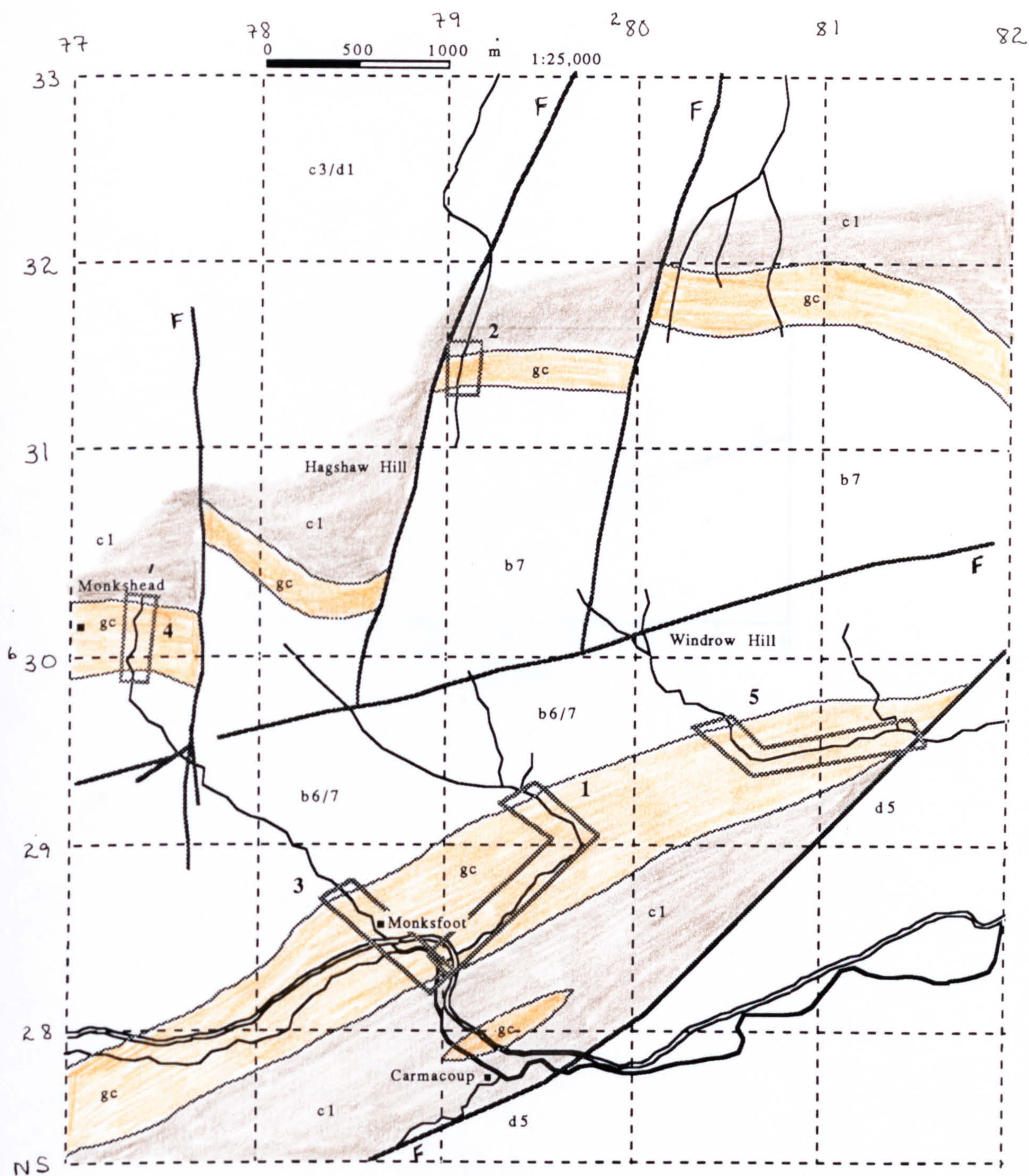


Fig. 3.2.1 Section locations for Greywacke Conglomerate, Hagshaw Hills

ornament as Fig. 3.1.7

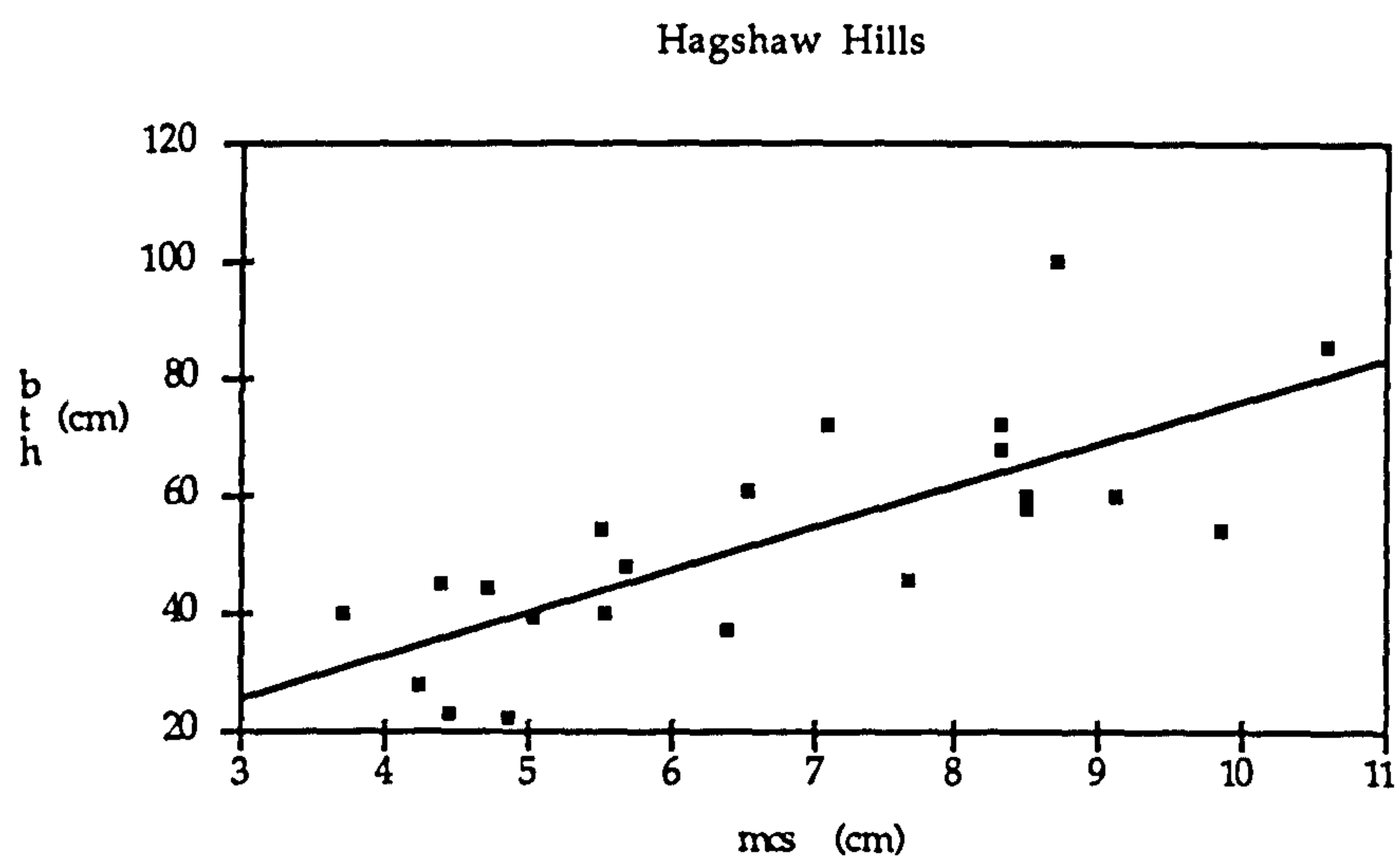


Fig. 3.2.2 MCS vs Bth linear regression, Hagshaw Hills Greywacke Conglomerate

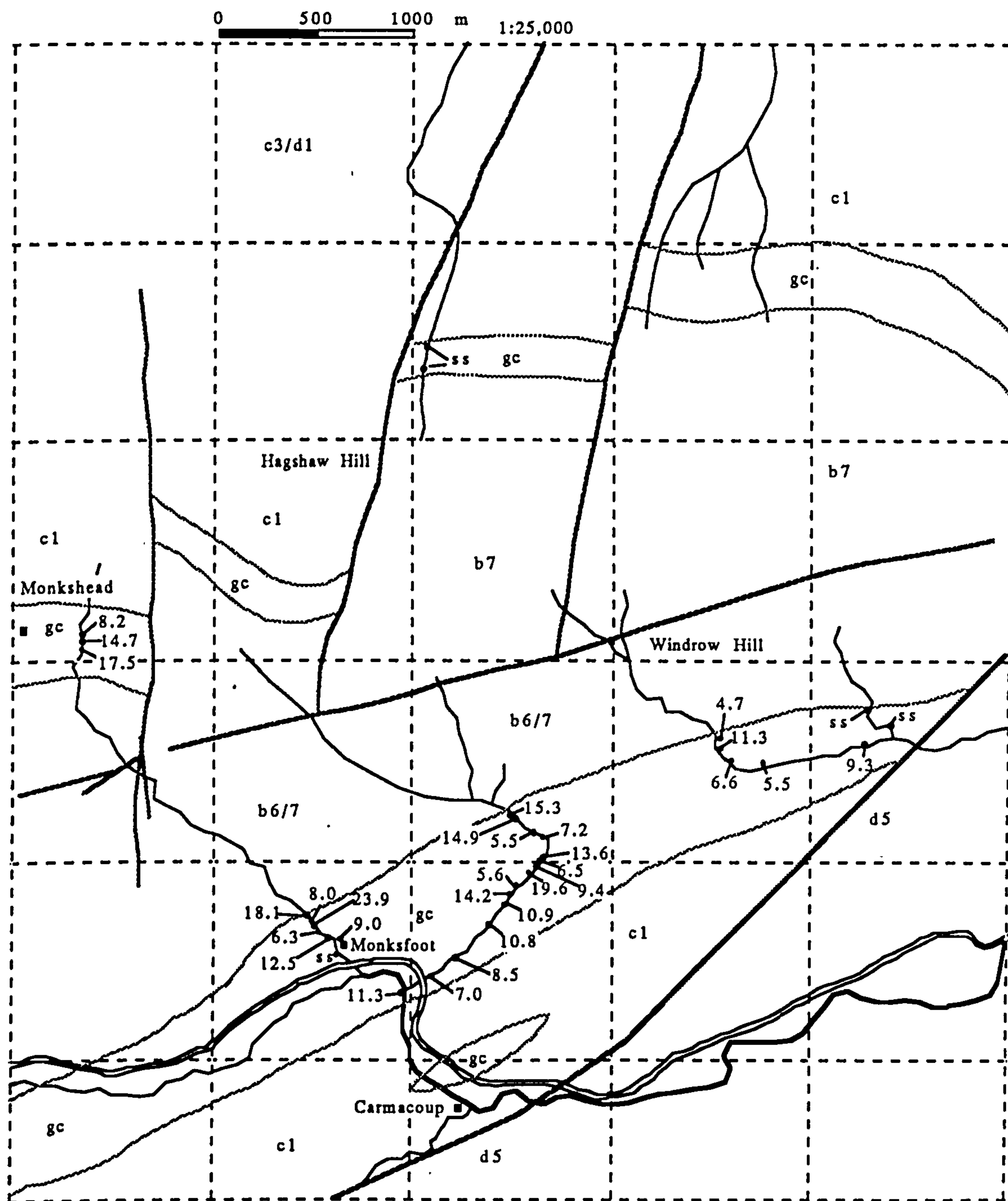


Fig. 3.2.3 Mean MCS in Greywacke Conglomerate, Hagshaw Hills

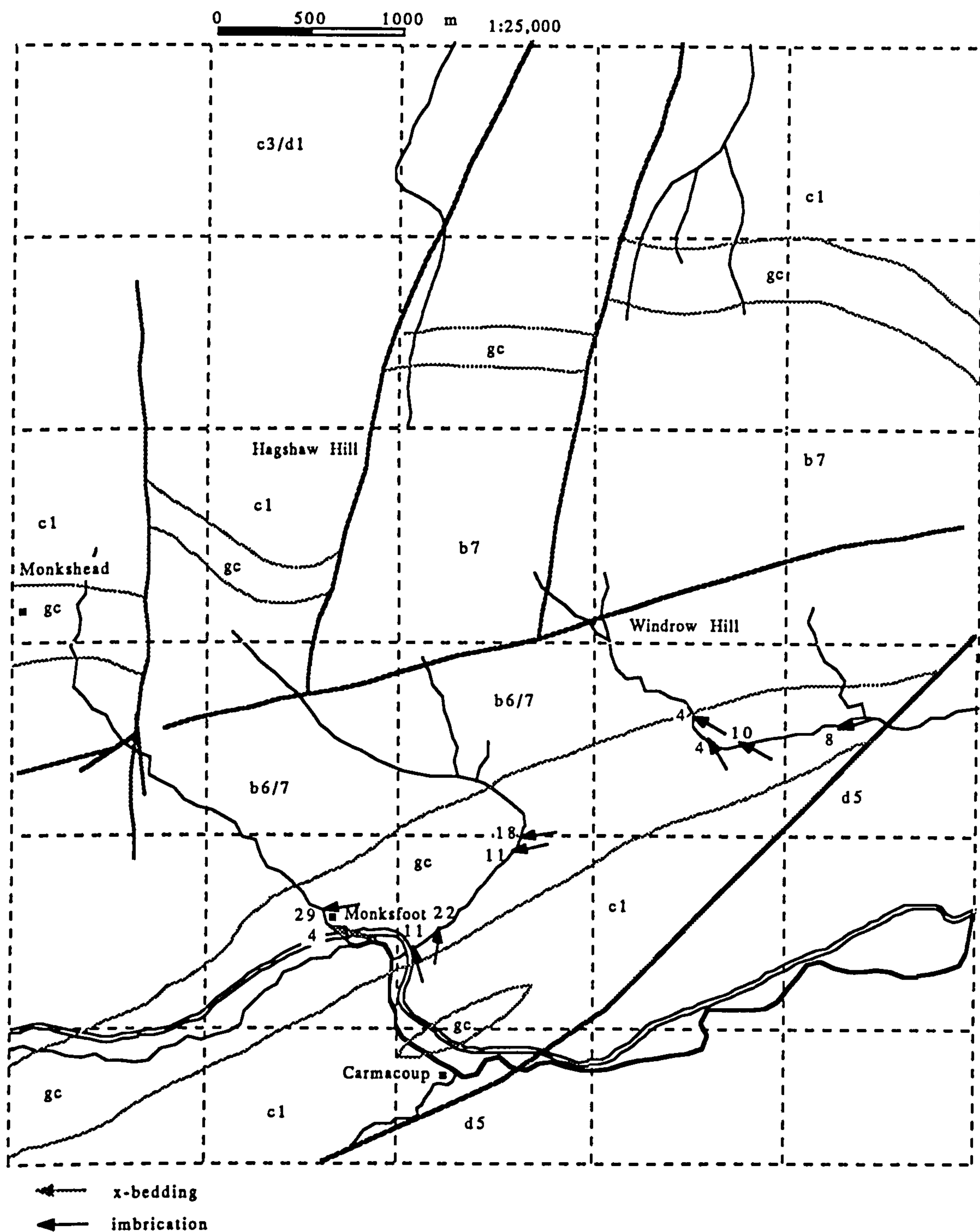


Fig. 3.2.4 Palaeoflow vectors for Greywacke Conglomerate, Hagshaw Hills

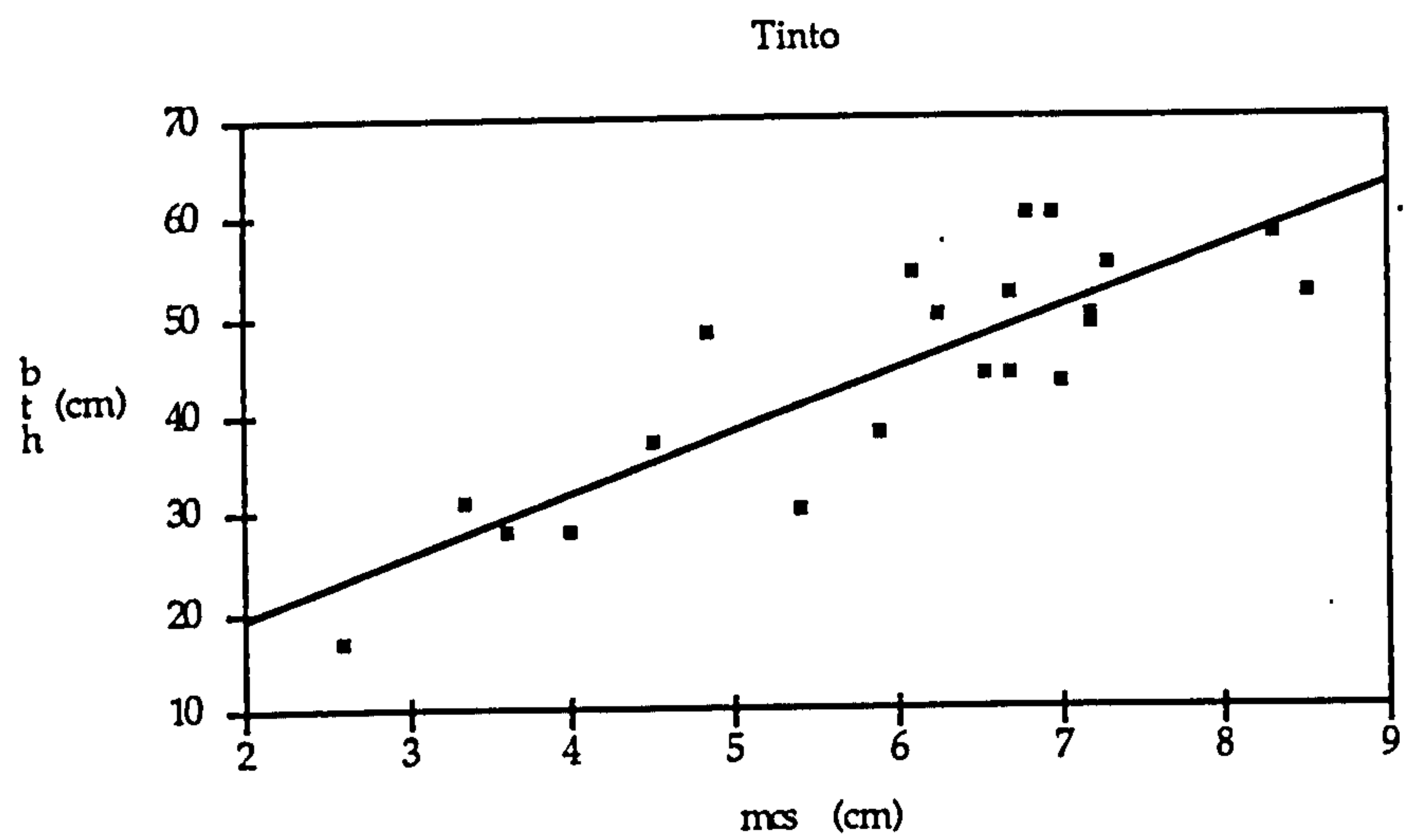


Fig. 3.3.1 MCs vs Bth linear regression, Tinto Greywacke Conglomerate

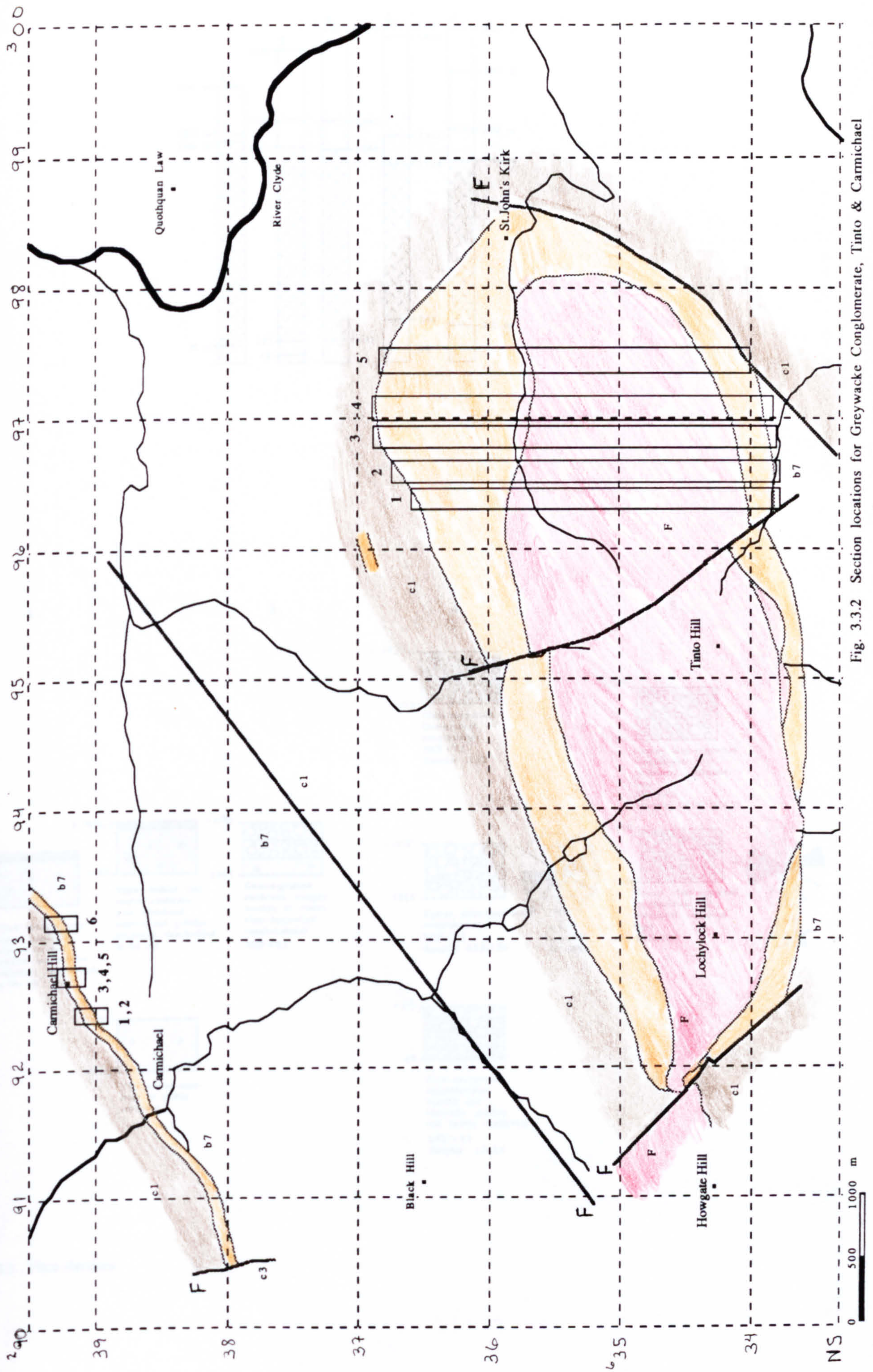


Fig. 3.3.2 Section locations for Greywacke Conglomerate, Tinto & Carmichael
ornament as in Fig. 3.1.7

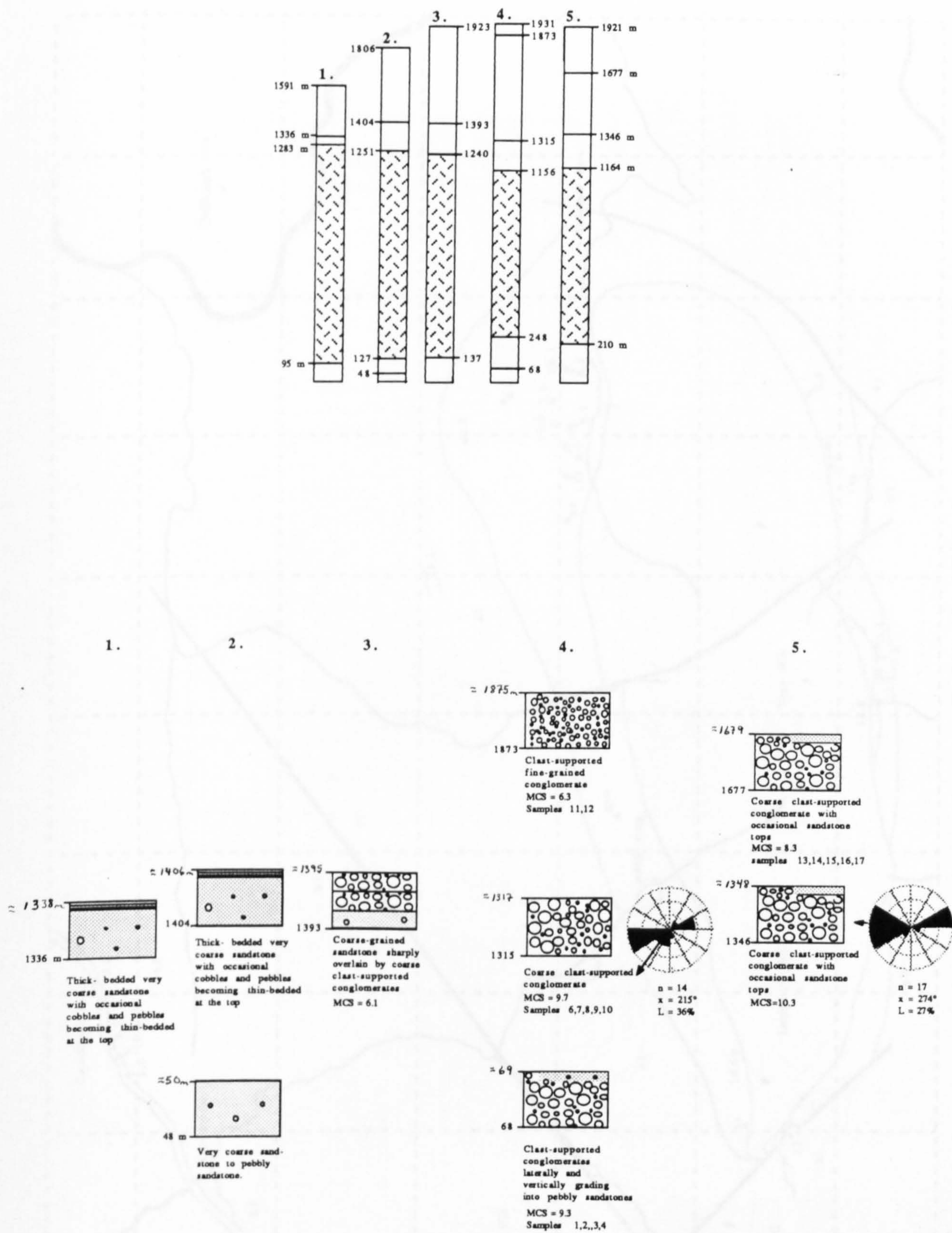


Fig. 3.3.3 Tinto Sections

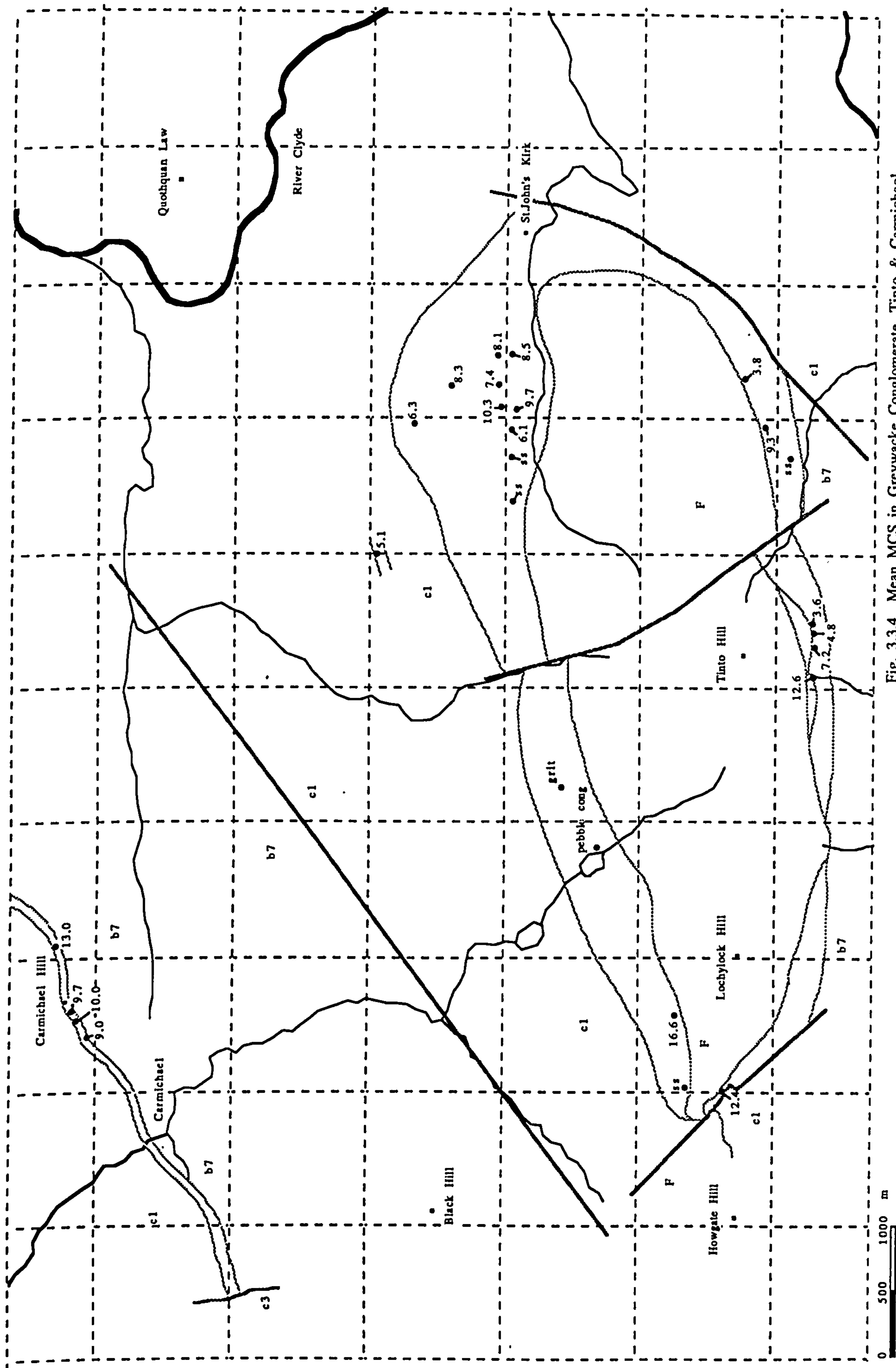
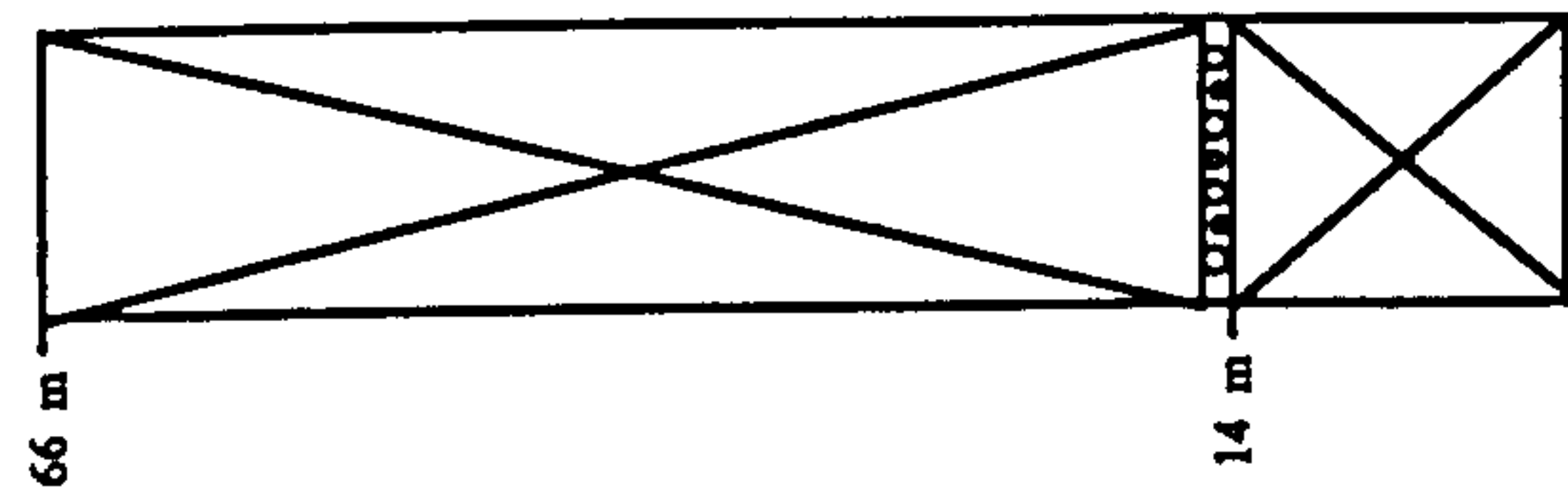


Fig. 3.3.4 Mean MCS in Greywacke Conglomerate, Tinto & Carmichael

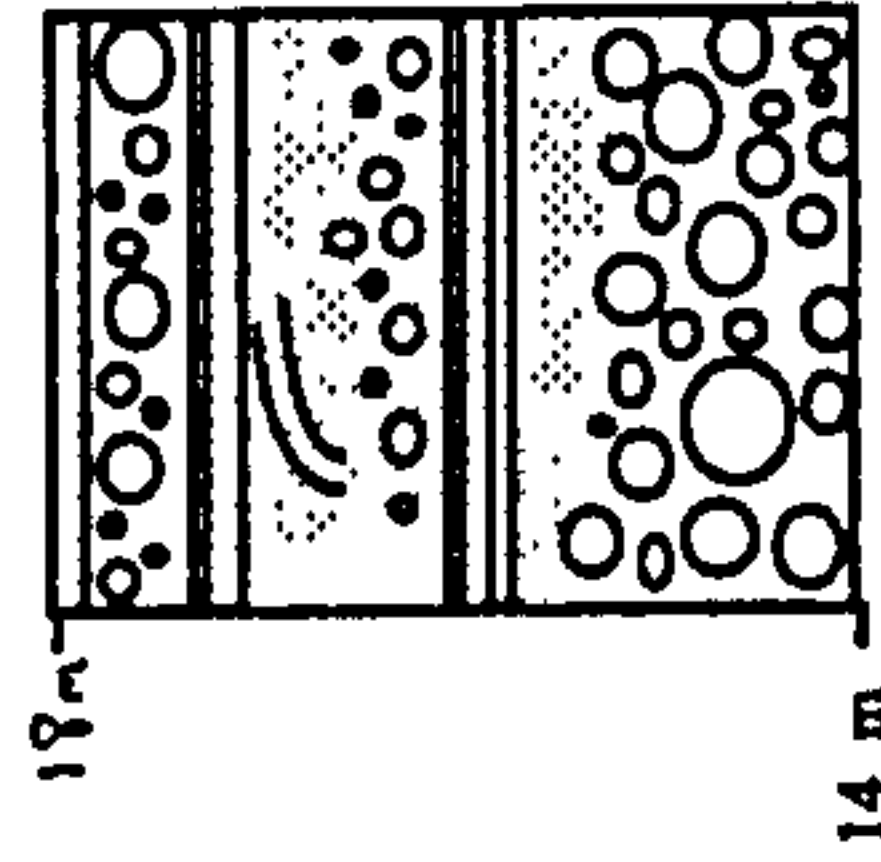
CARMICHAEL



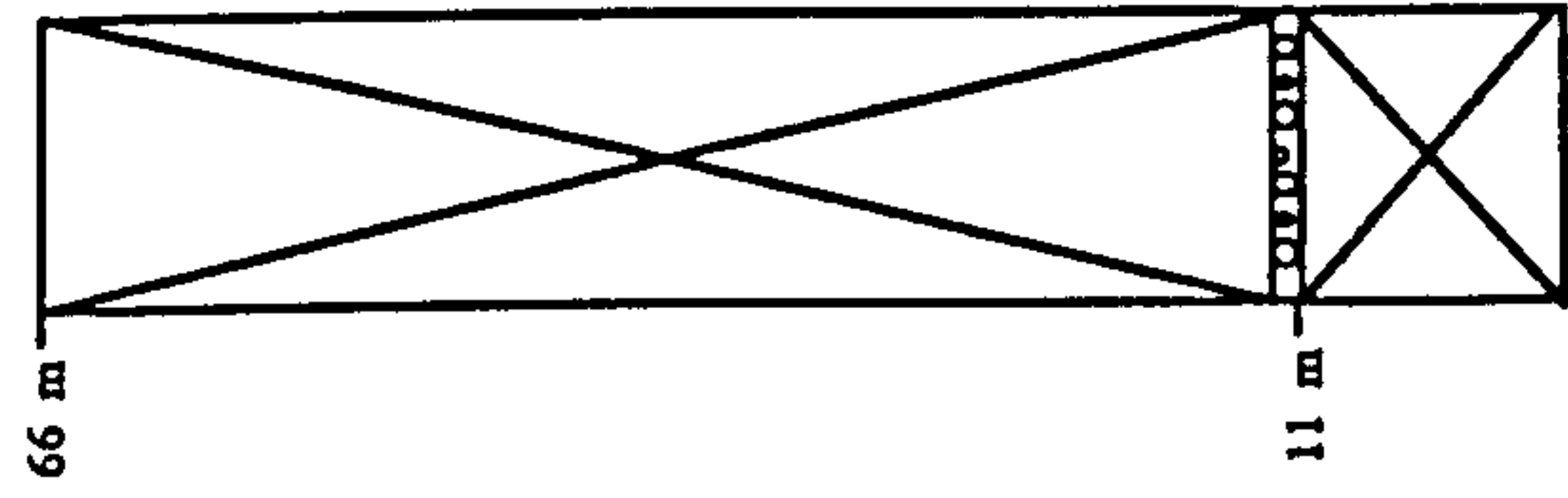
n = 12
x = 248°
L = 59%

(1), (2)

MCS (cm) = 8.7

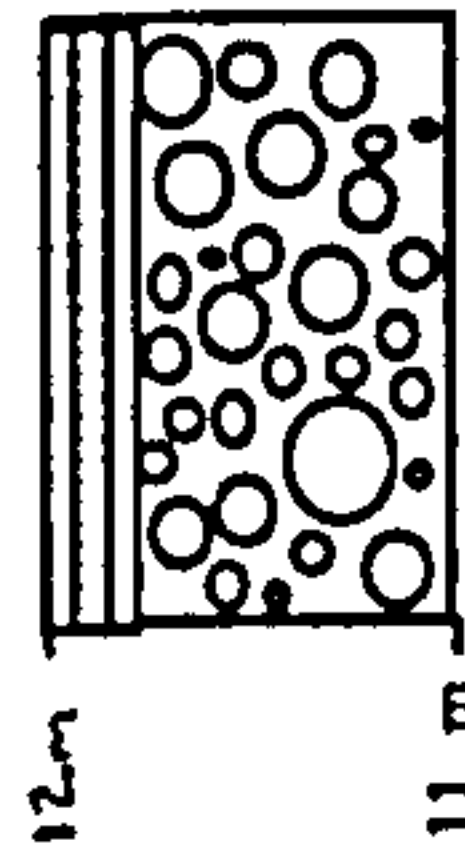


coarse clast-supported conglomerate grading into coarse - very coarse sandstone. Sandstone overlain by thin-bedded coarse sandstone. Repetition of conglomerate and sandstone with occasional small to medium scale planar cross-bedding in the sandstones.

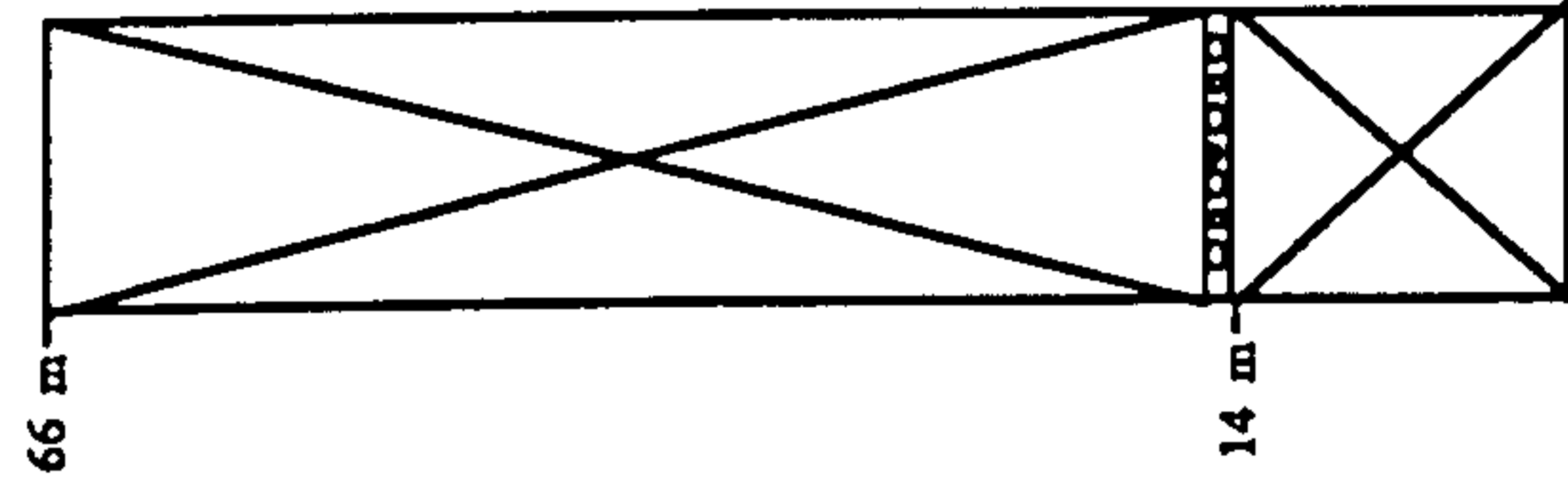


(3)

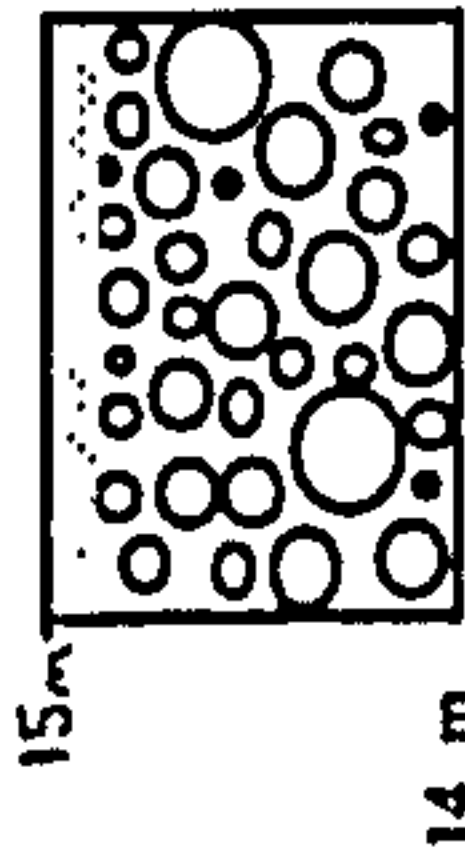
MCS (cm) = 10



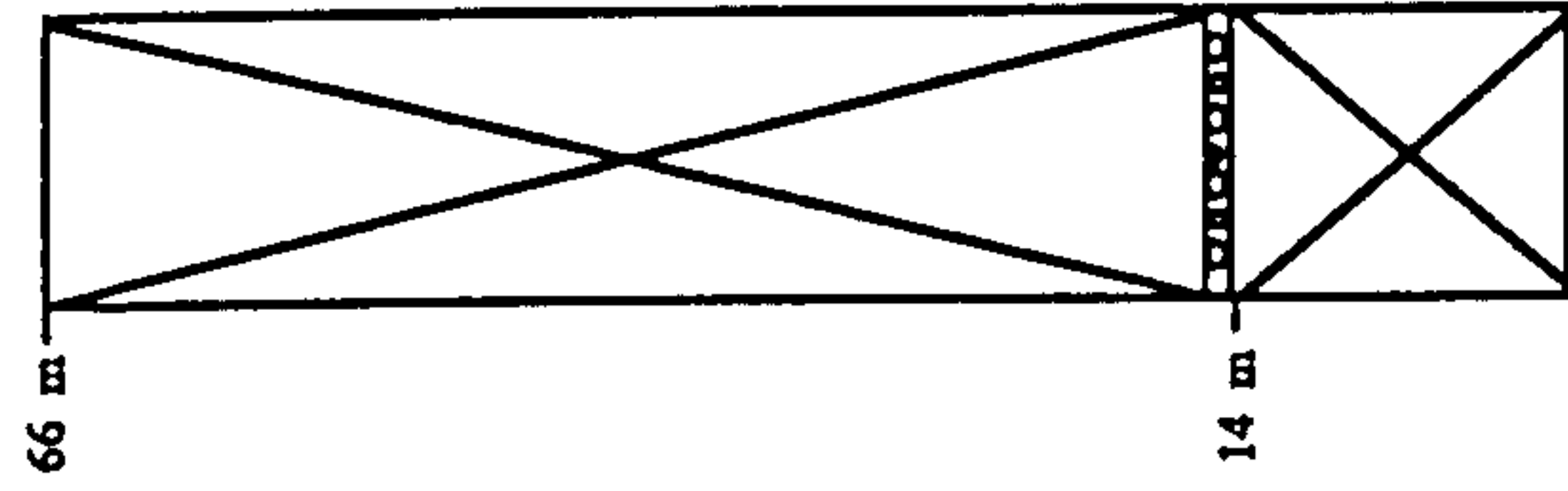
Thin bedded coarse sandstone sharply overlying coarse unstratified conglomerate



(4)

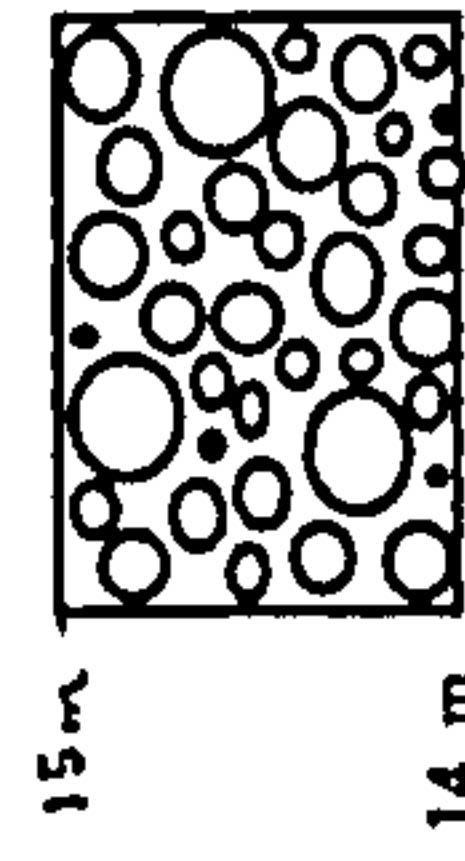


Coarse clast supported conglomerate grading upward into very coarse sandstone

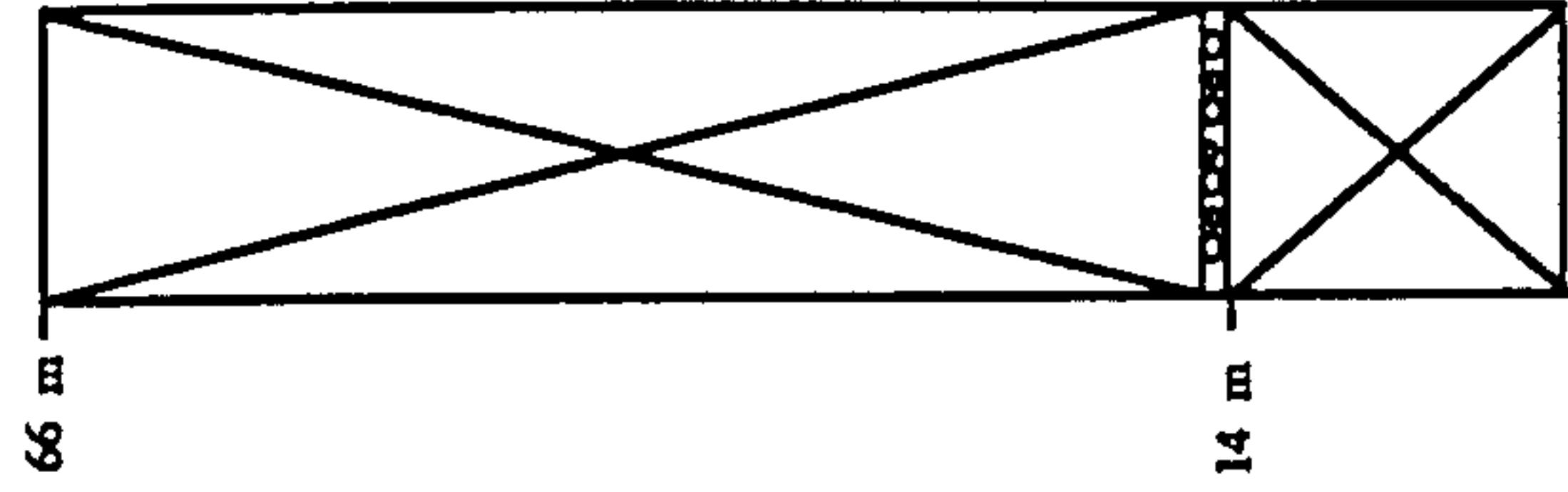


(5)

MCS (cm) = 9.7

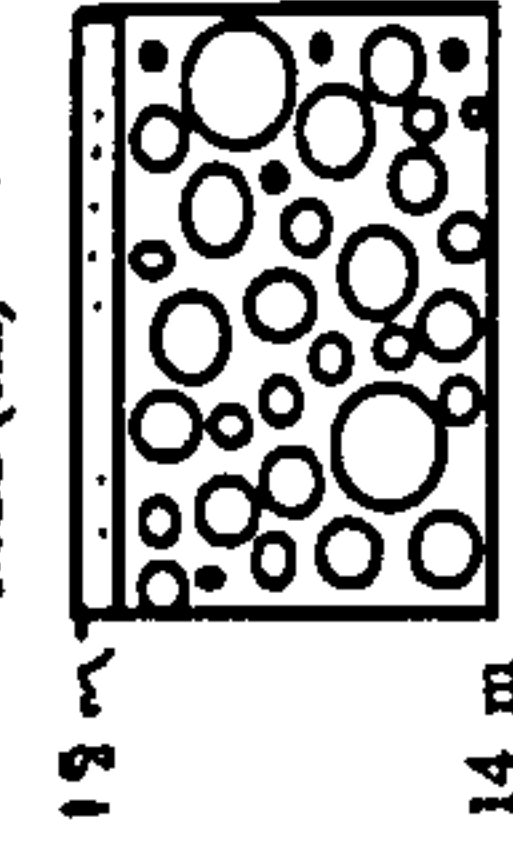


Coarse unstratified clast-supported conglomerate



(6)

MCS (cm) = 13



Coarse unstratified clast-supported conglomerate with occasional sandstone tops.



n = 27
x = 227°
L = 47%

Fig. 3.3.5 Carmichael Sections

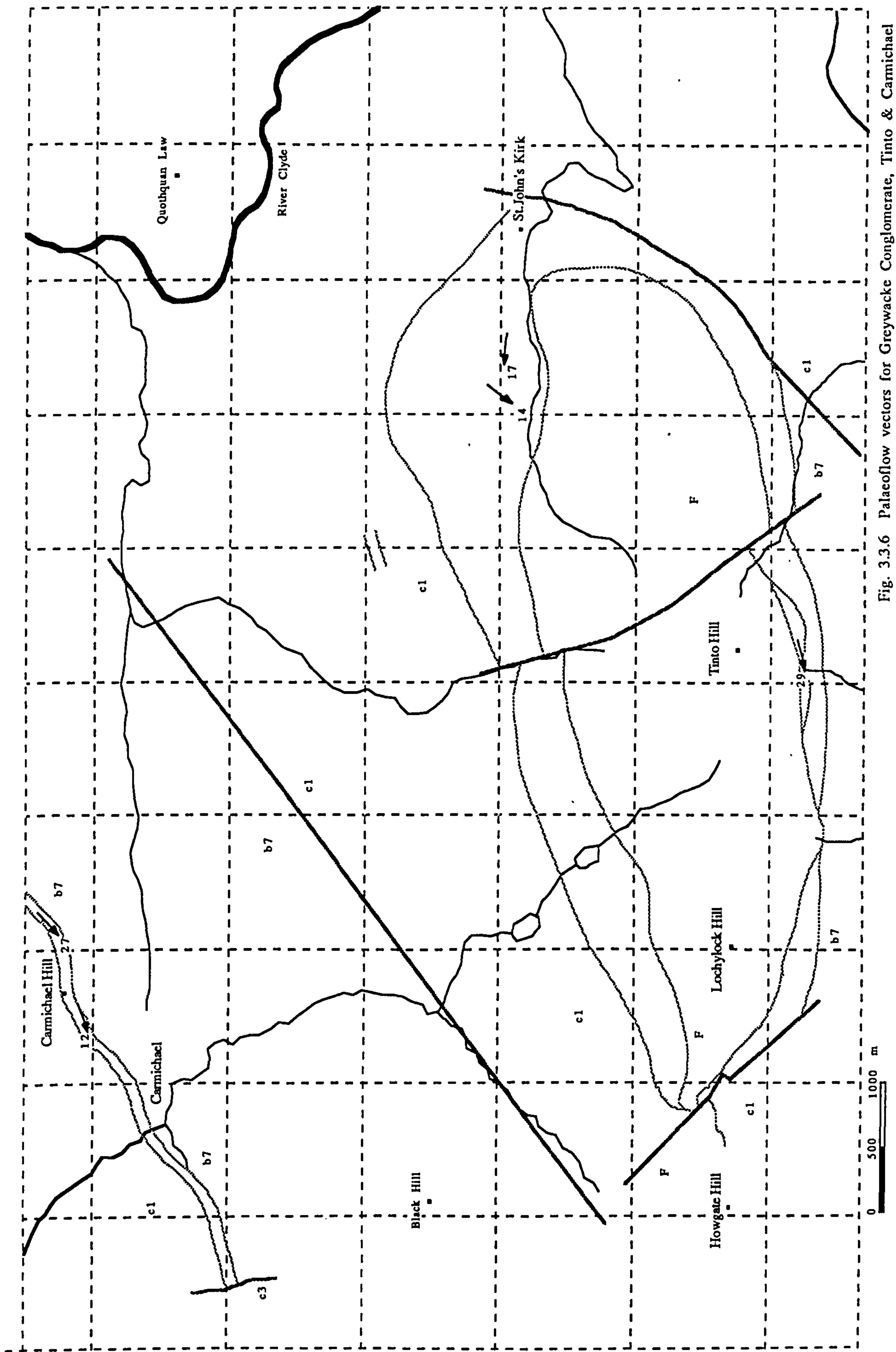


Fig. 3.3.6 Palaeoflow vectors for Greywacke Conglomerate, Tinto & Carmichael

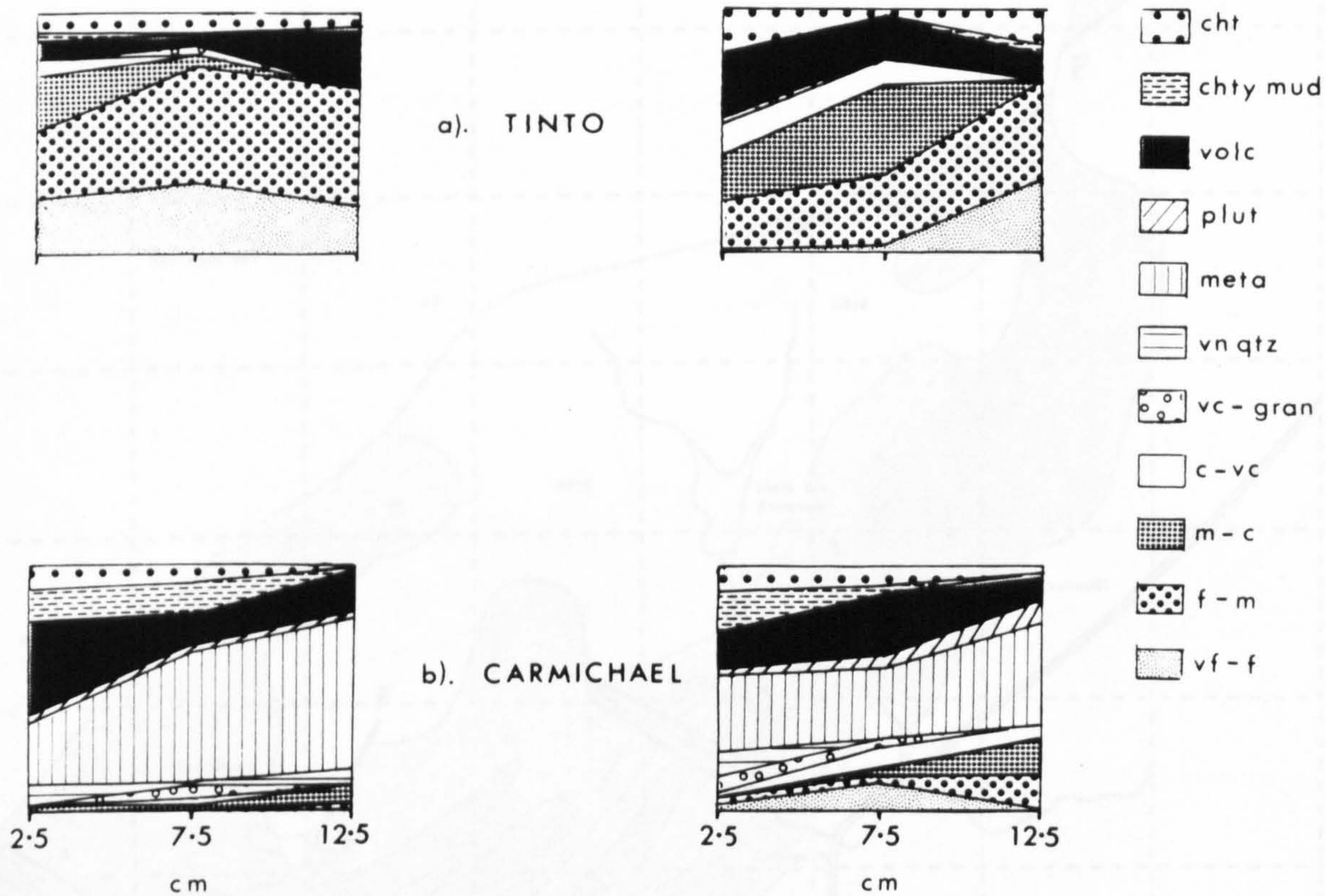


Fig 3.3.7 Clast composition

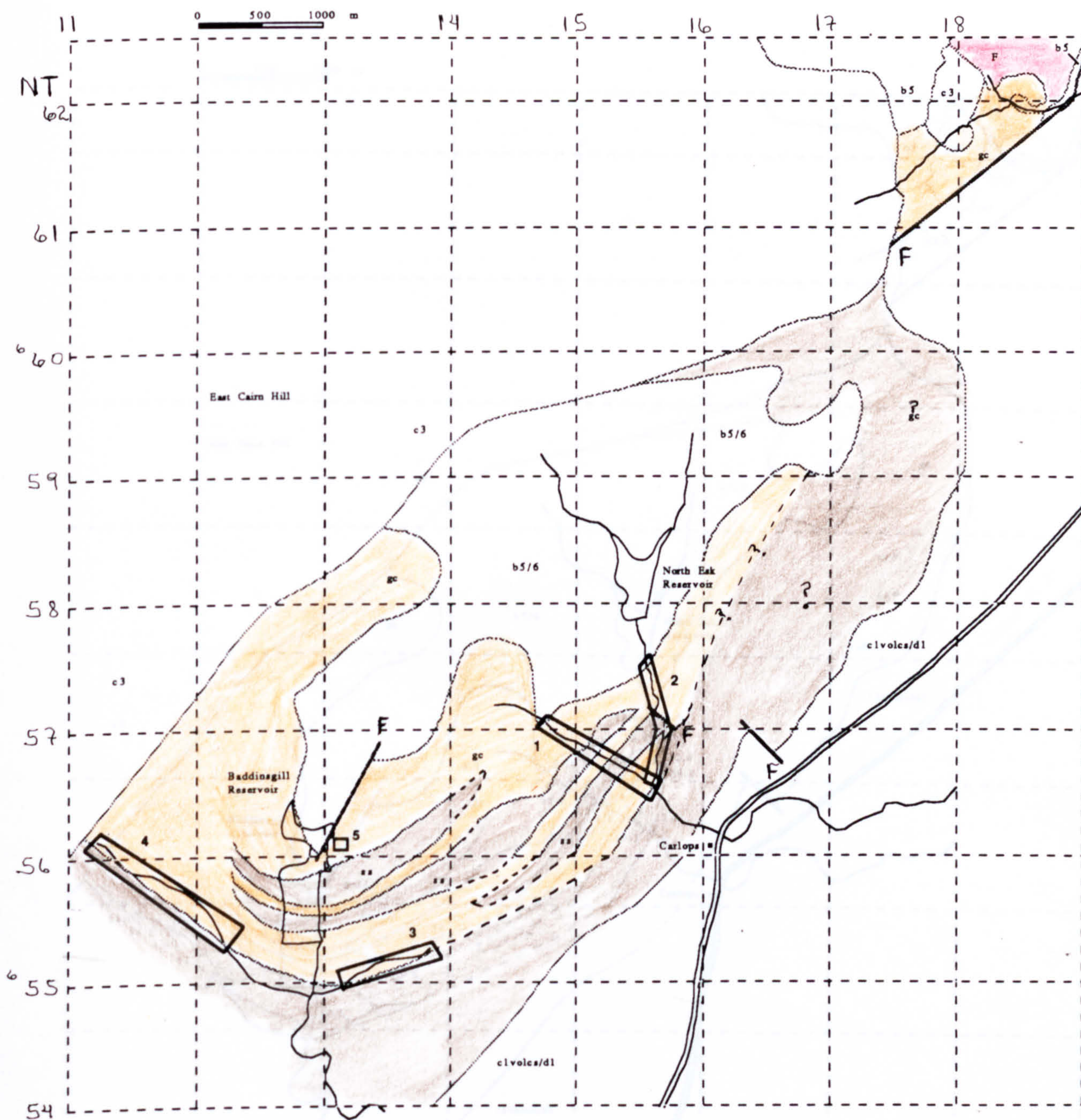


Fig. 3.4.1 Section locations for Greywacke Conglomerate, North Esk

ornament as in Fig. 3.1.7.

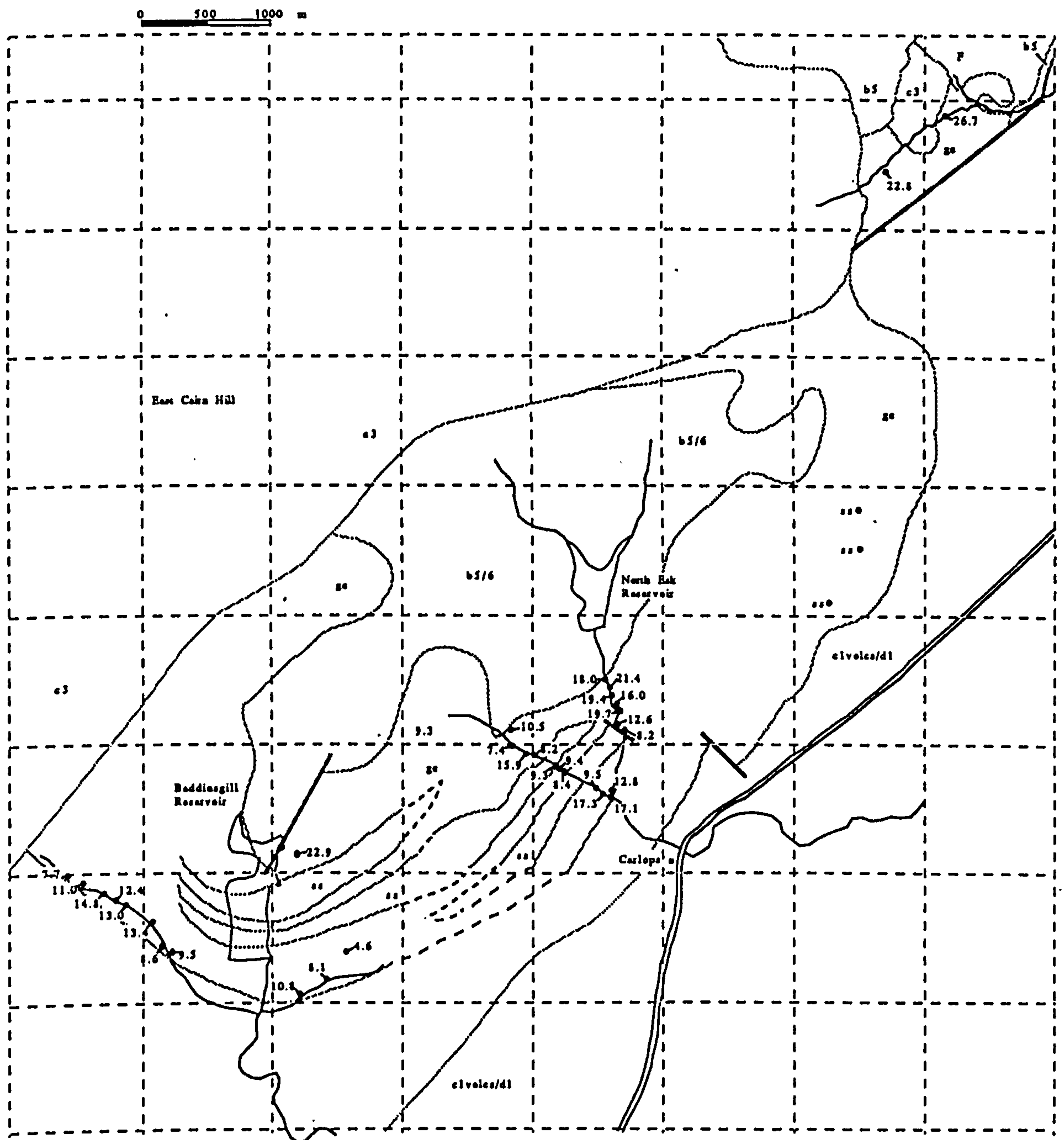


Fig. 3.4.2 Mean MCS in Greywacke Conglomerate, North Esk

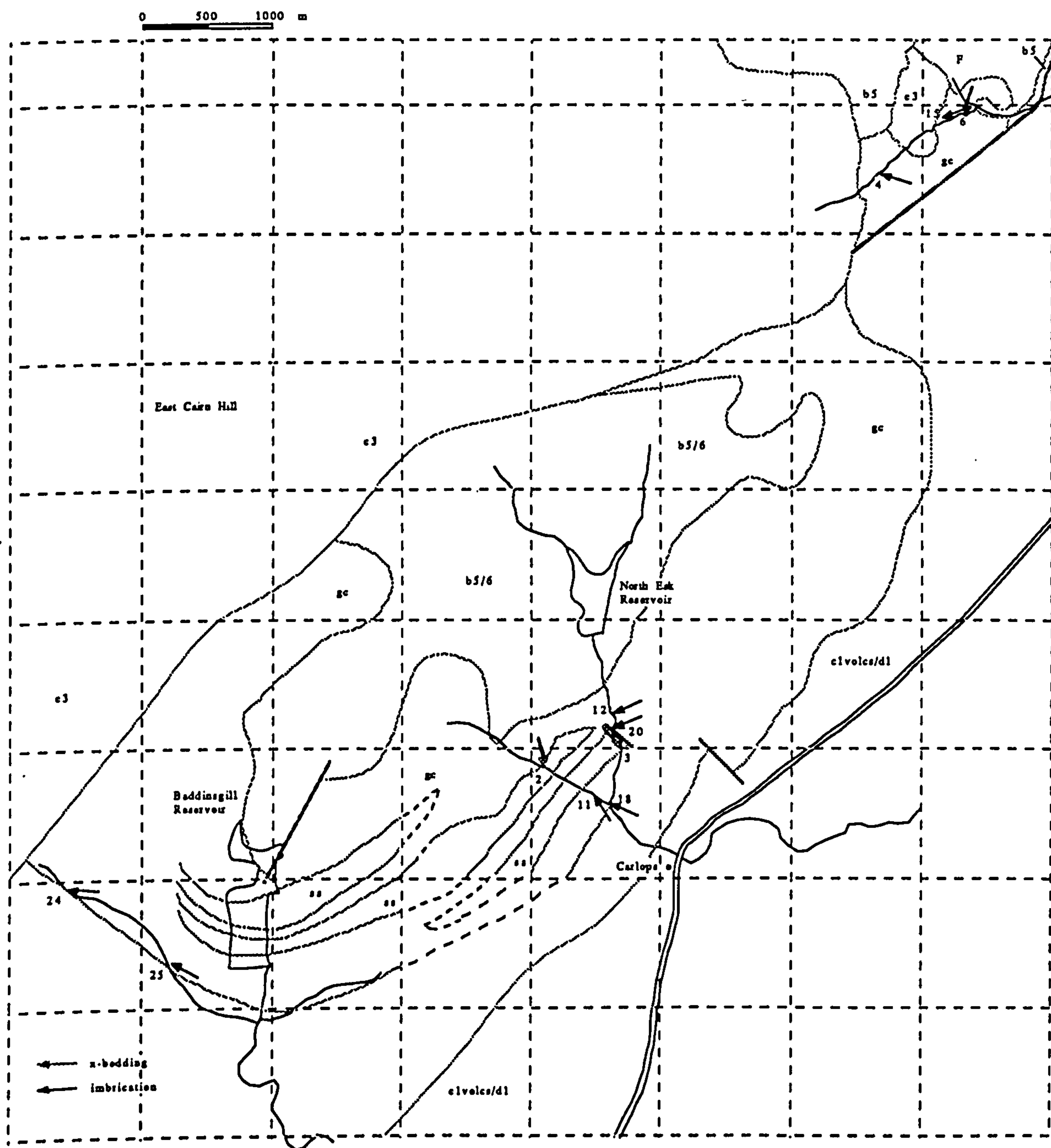


Fig. 3.4.3 Palaeoflow vectors for Greywacke Conglomerate, North Esk

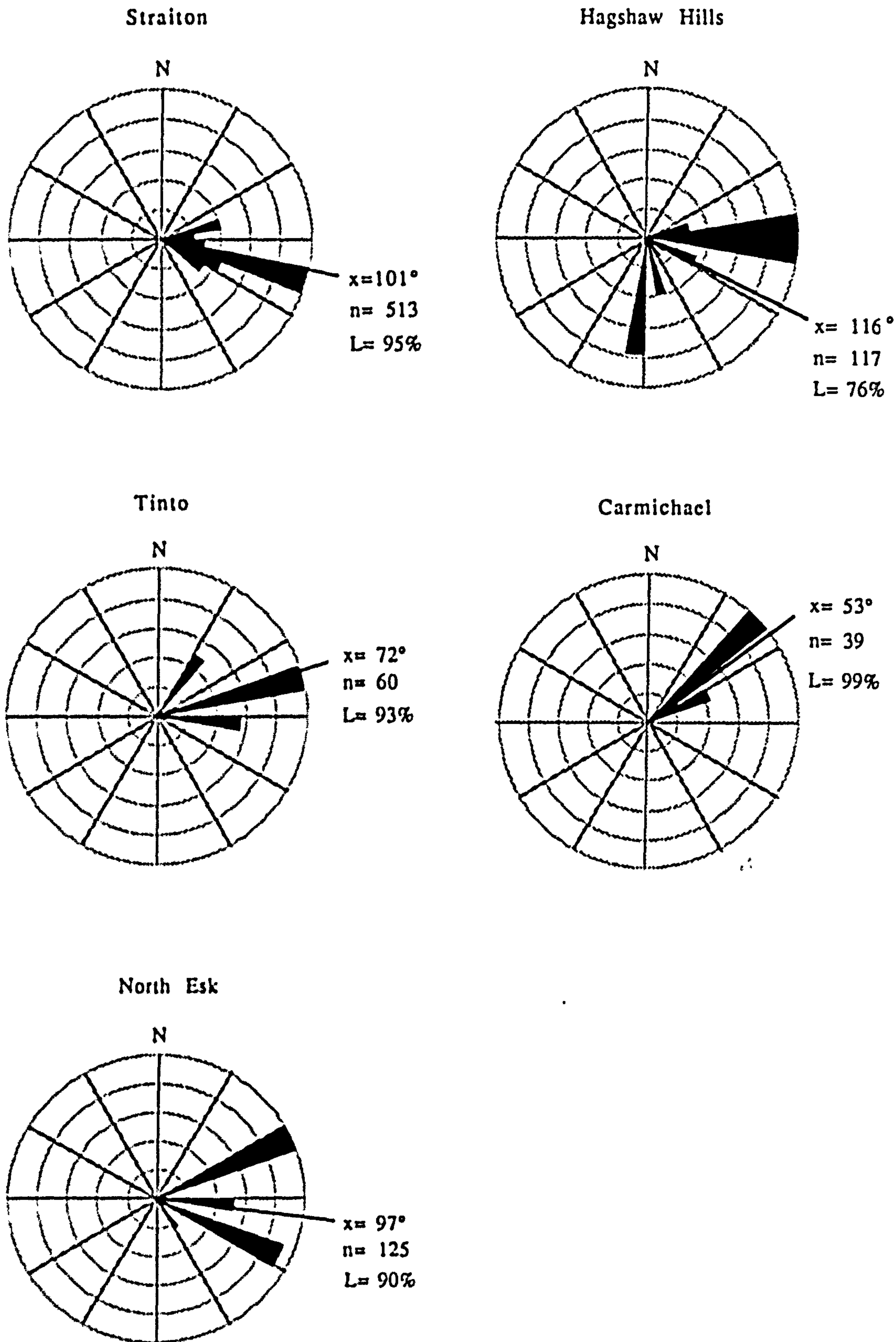
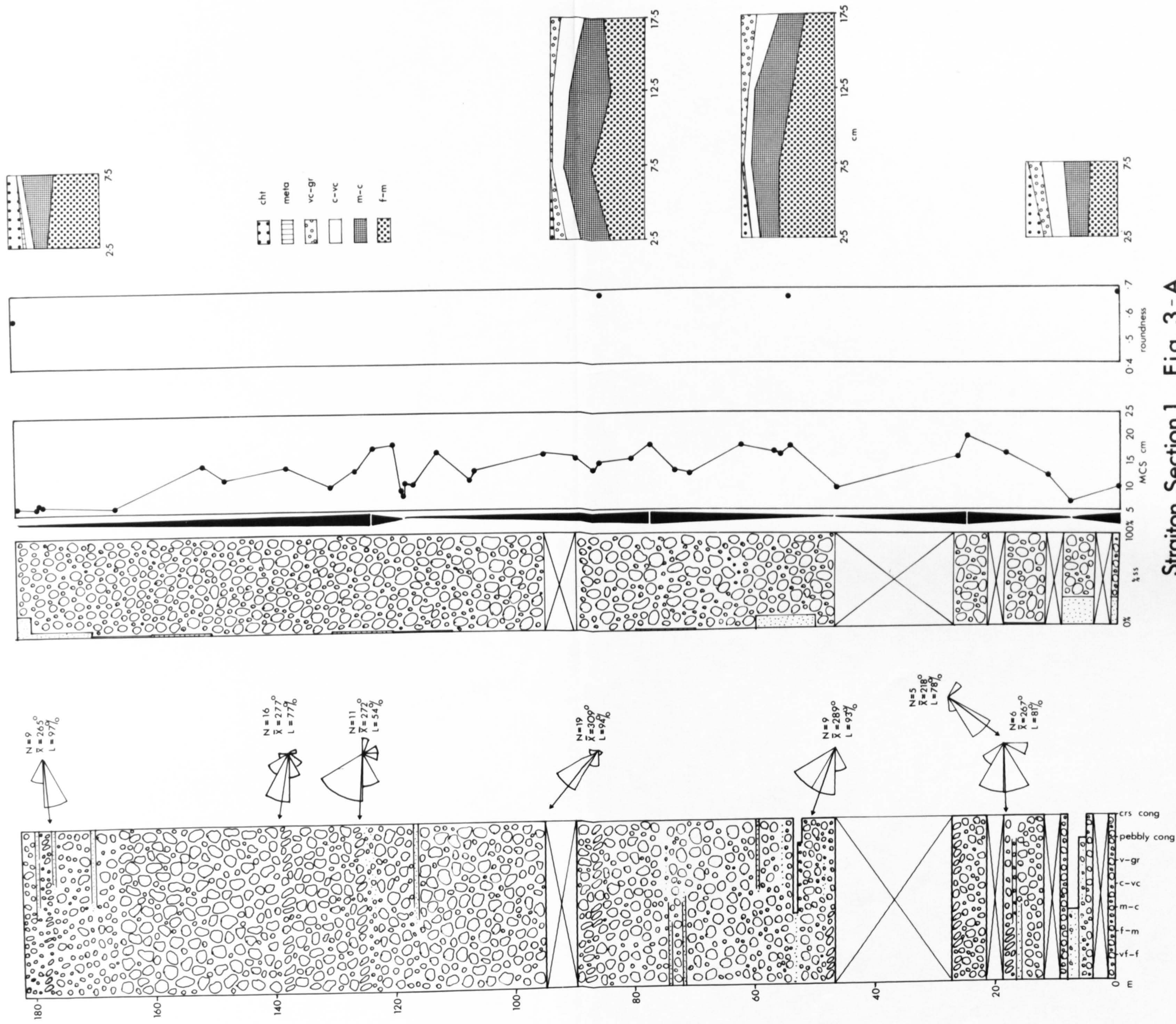
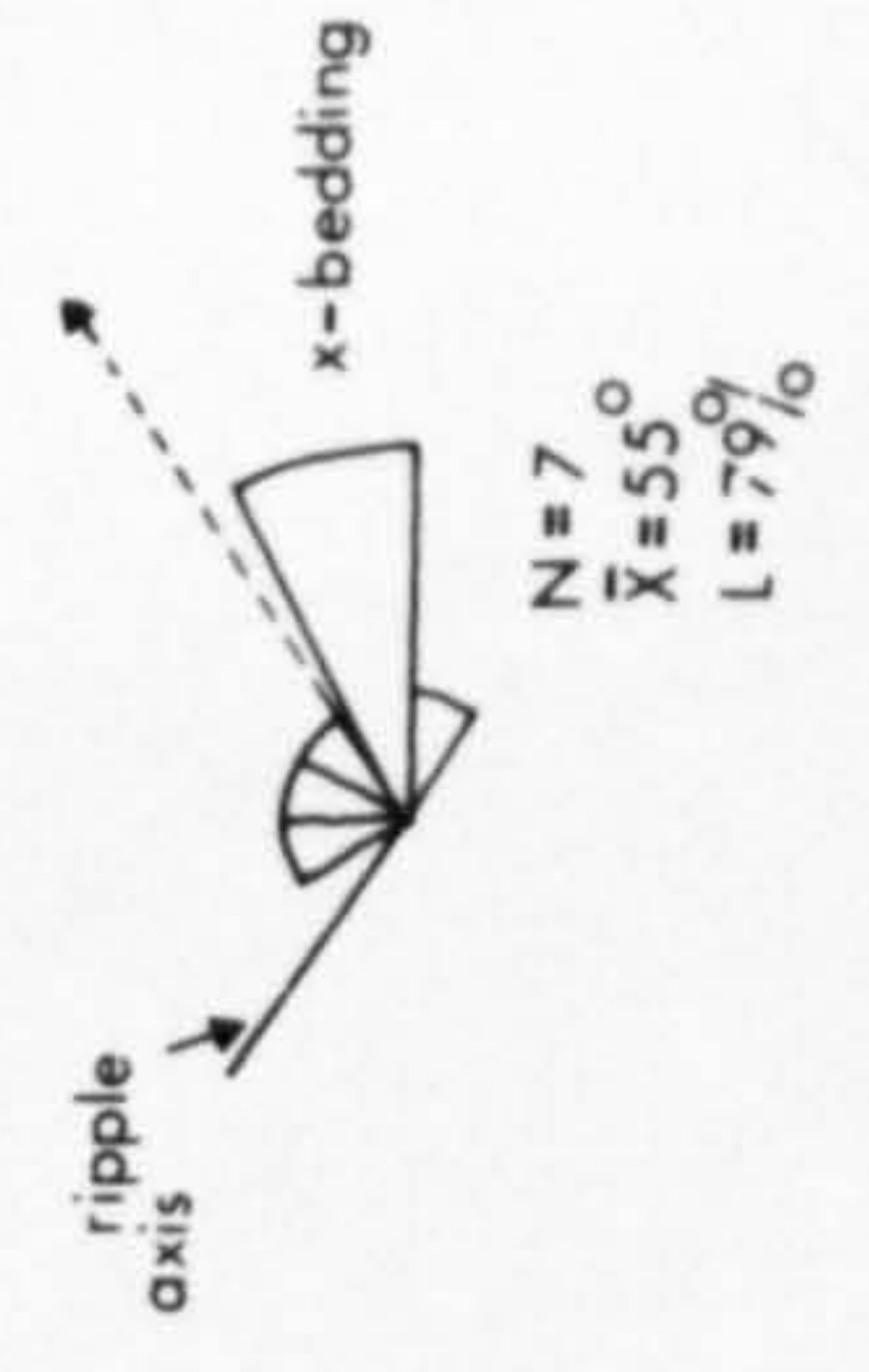
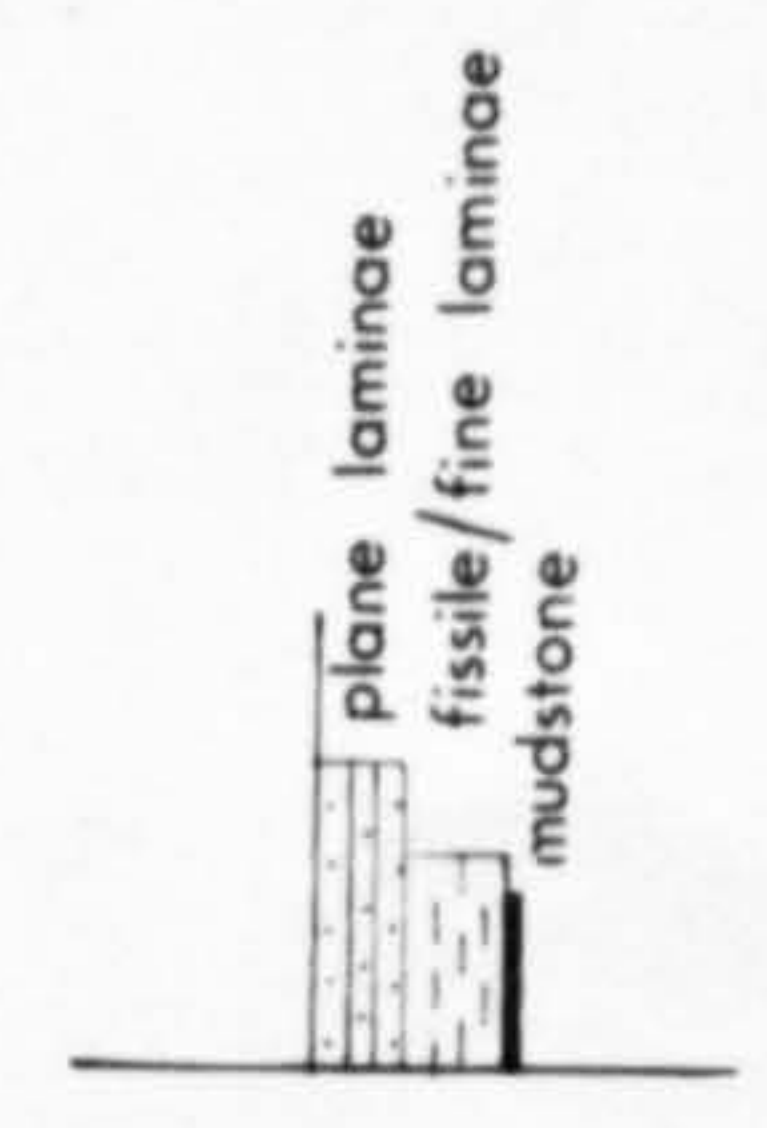
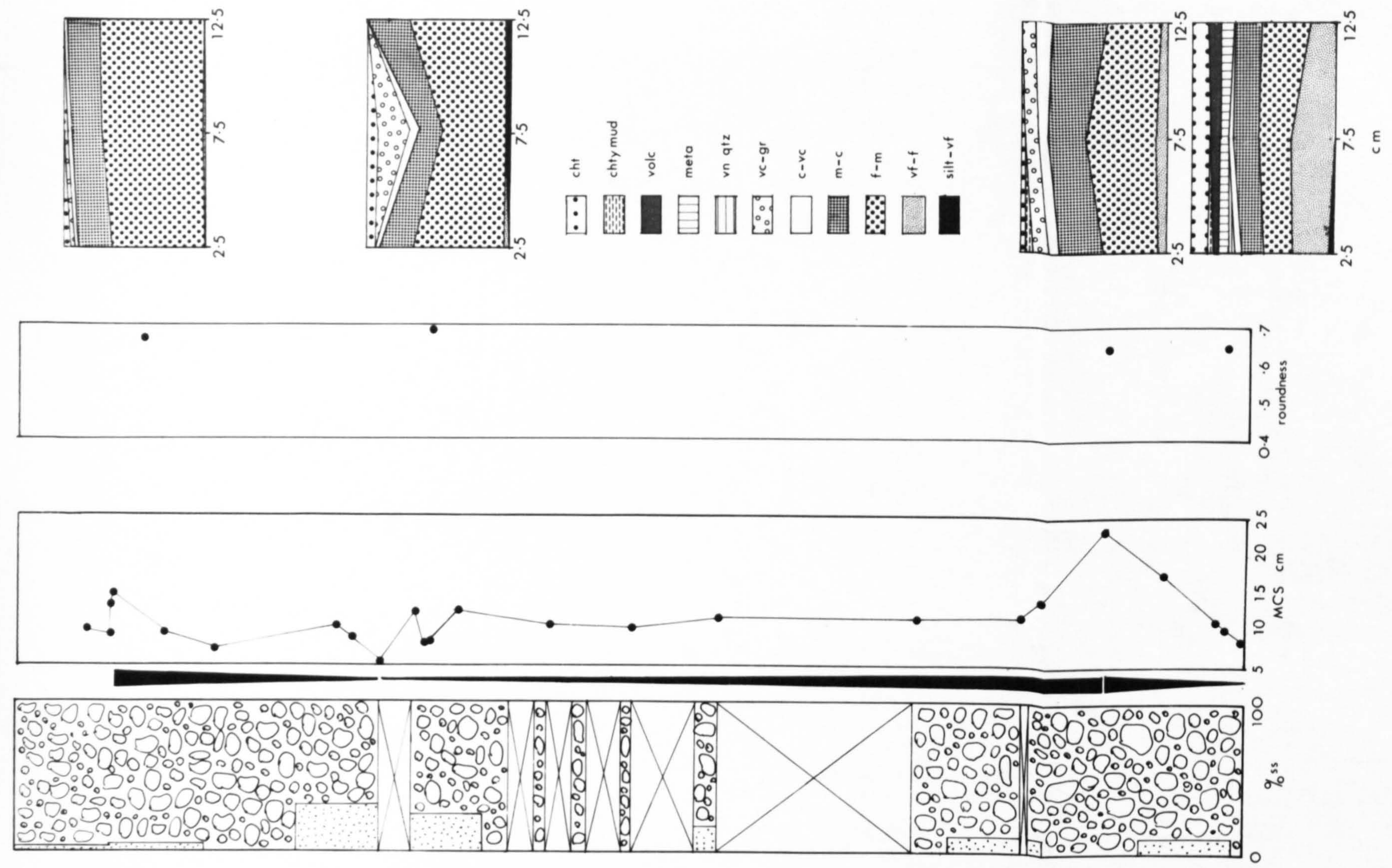
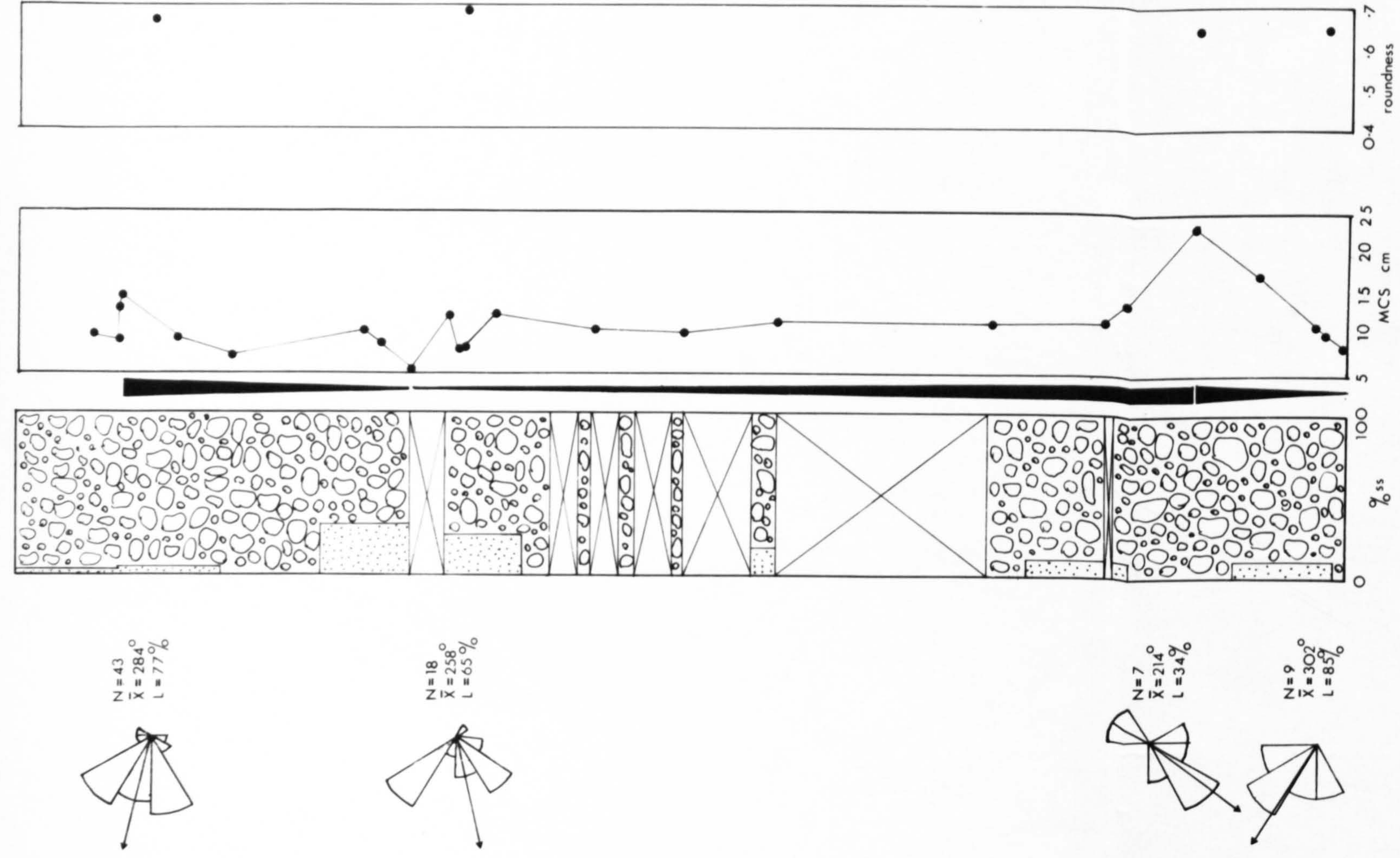
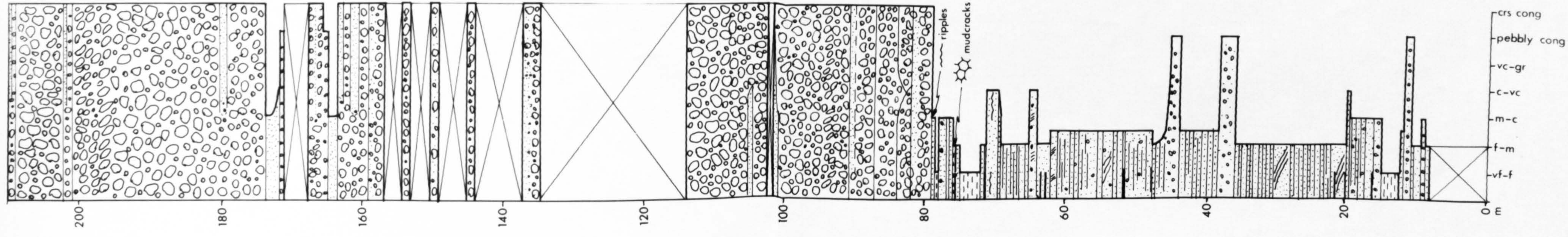


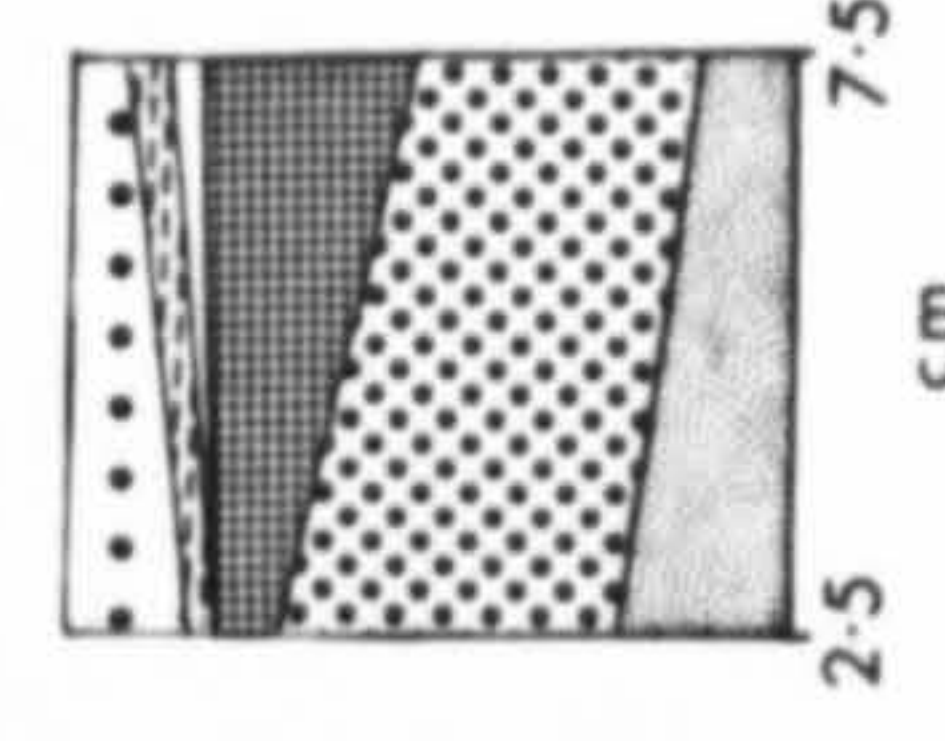
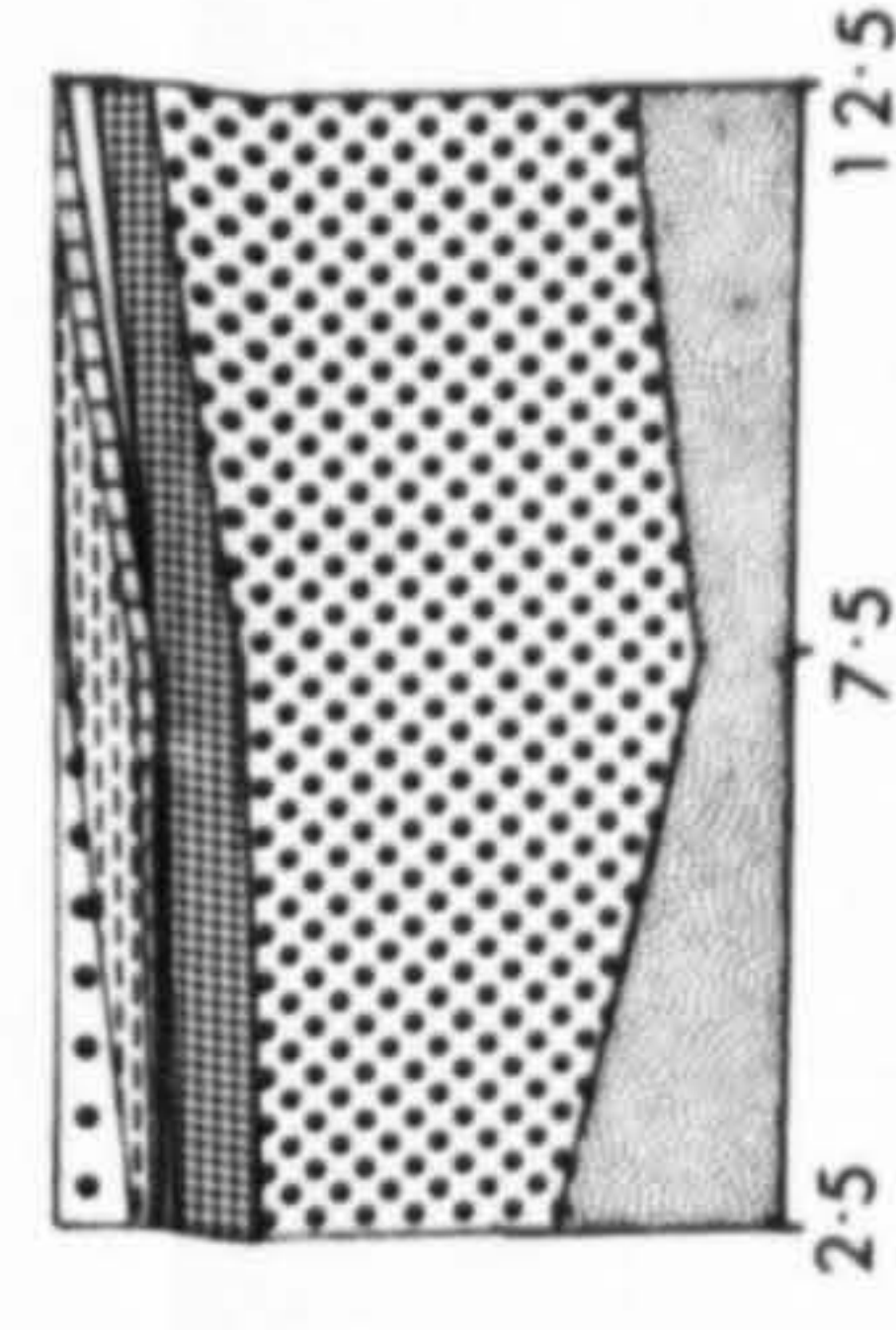
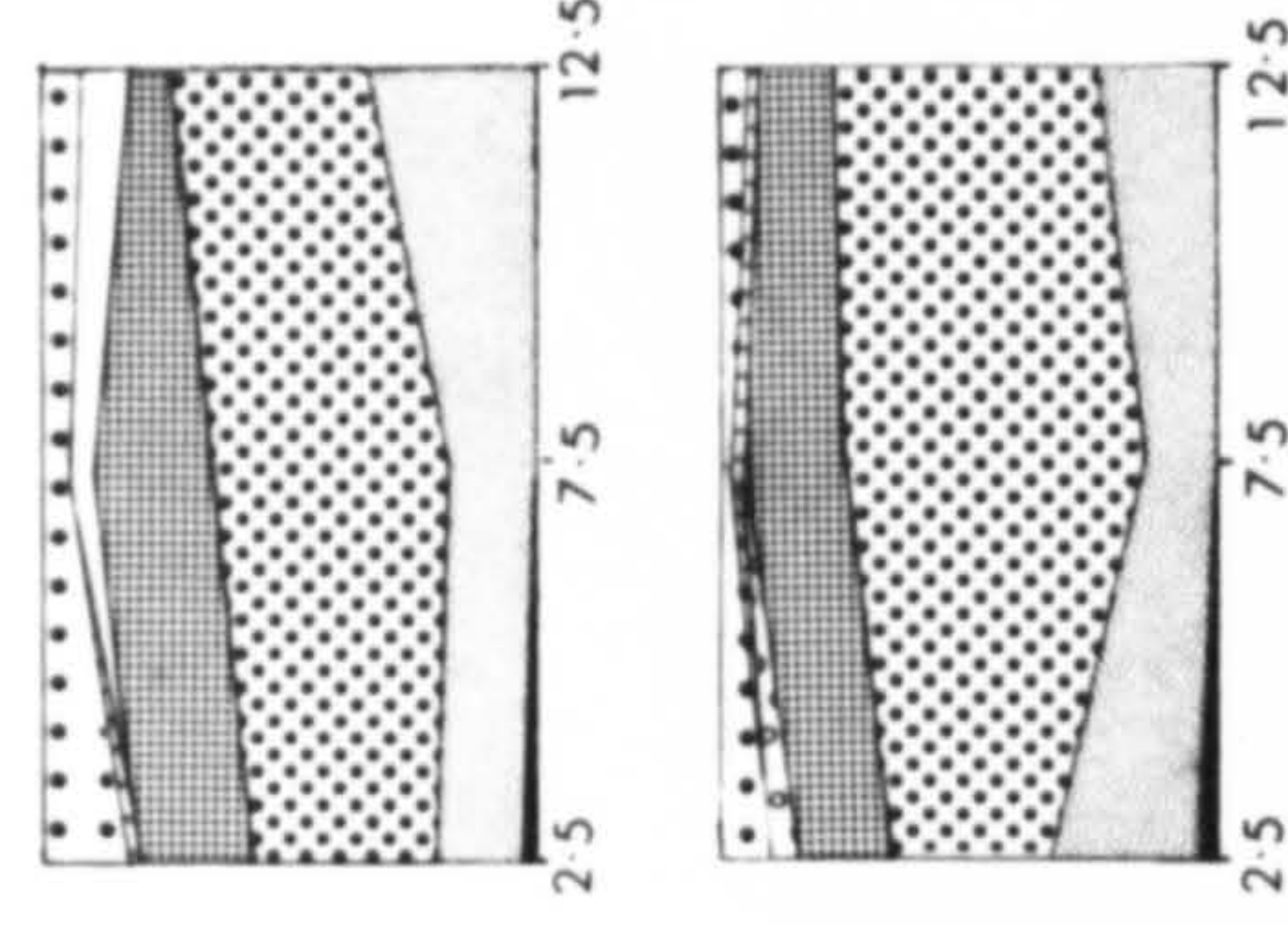
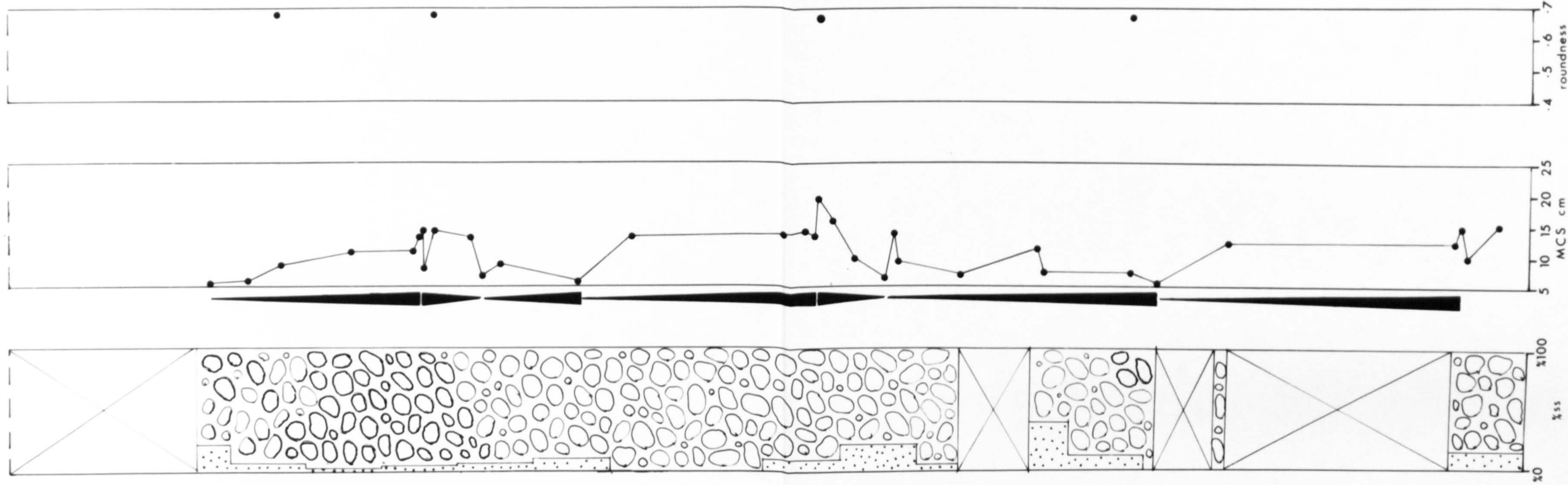
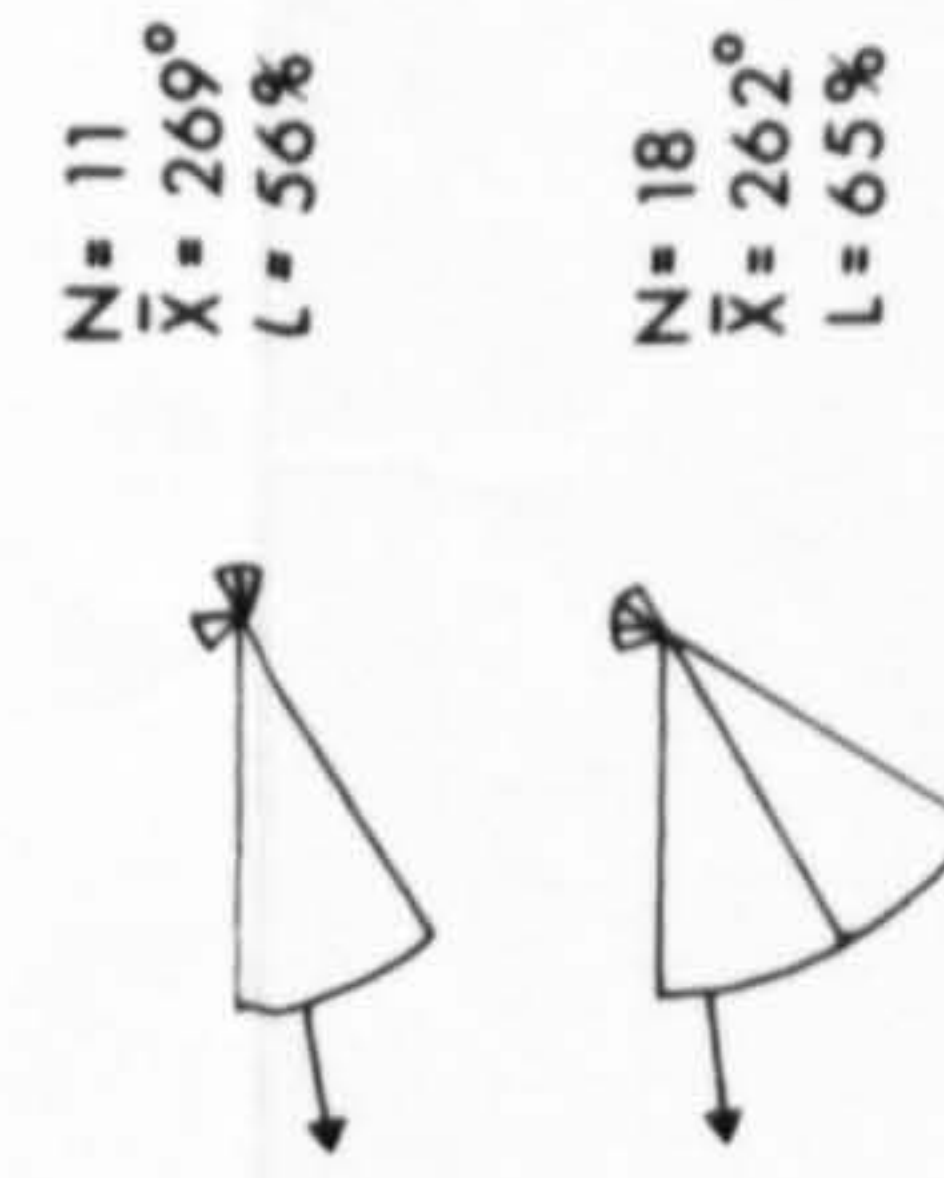
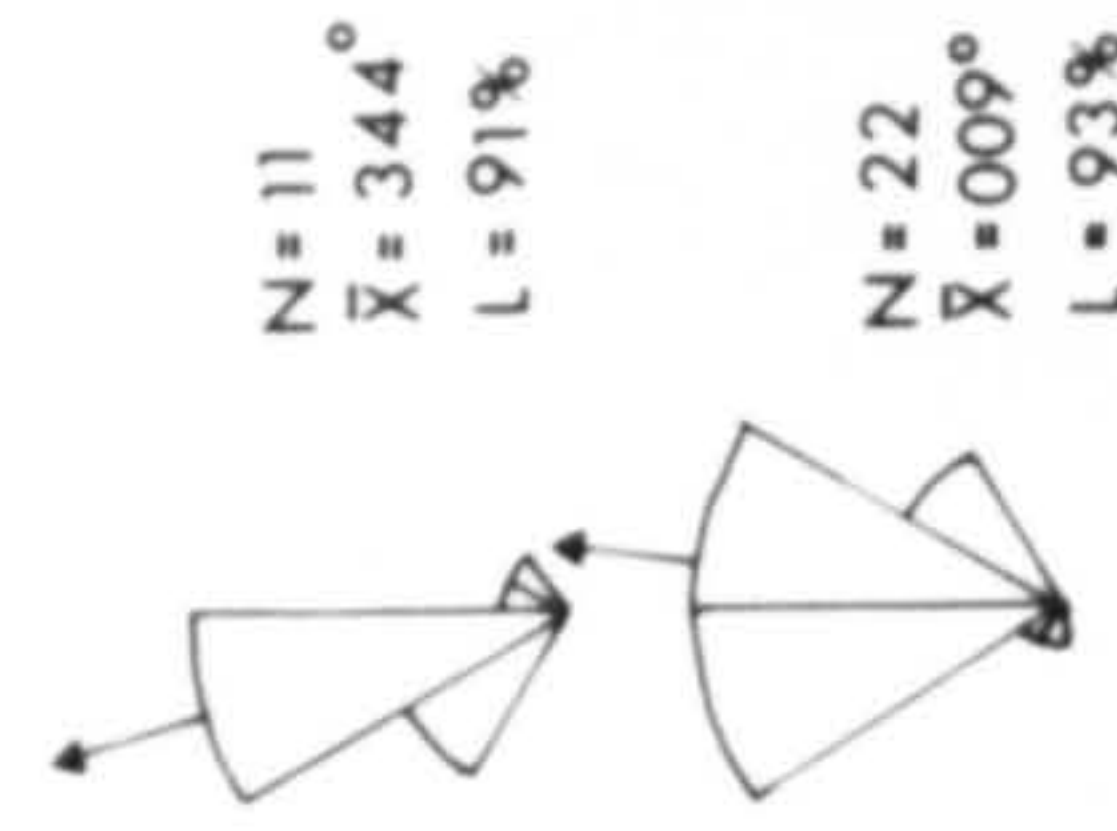
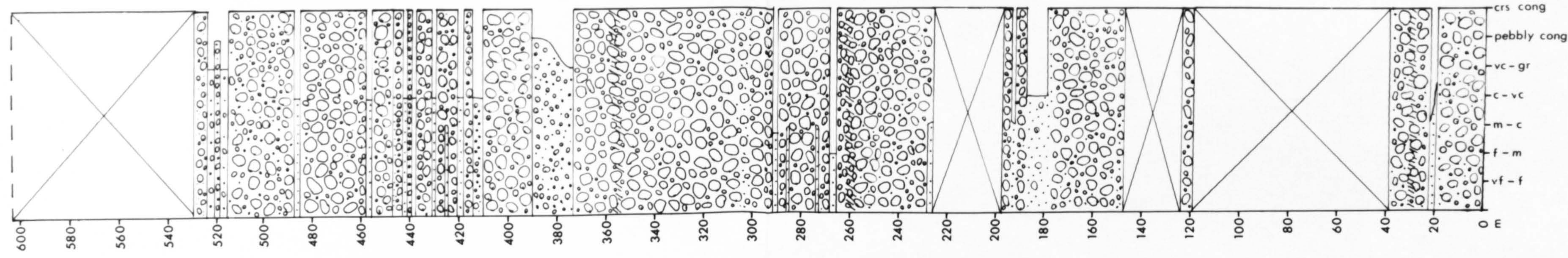
Fig. 3.5.1 Source direction from imbrication in Greywacke Cong.



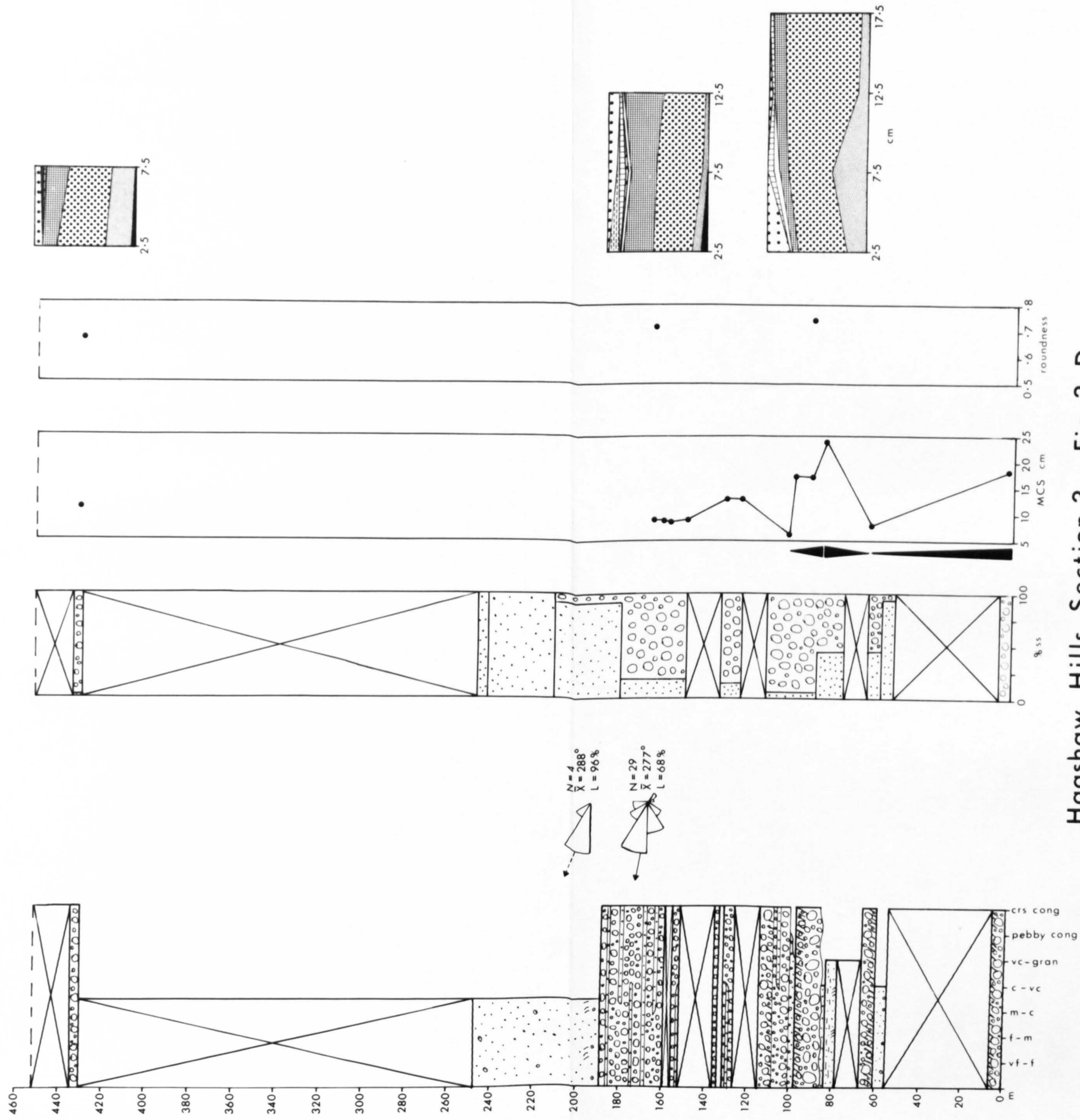
Straiton Section 1 Fig. 3-A



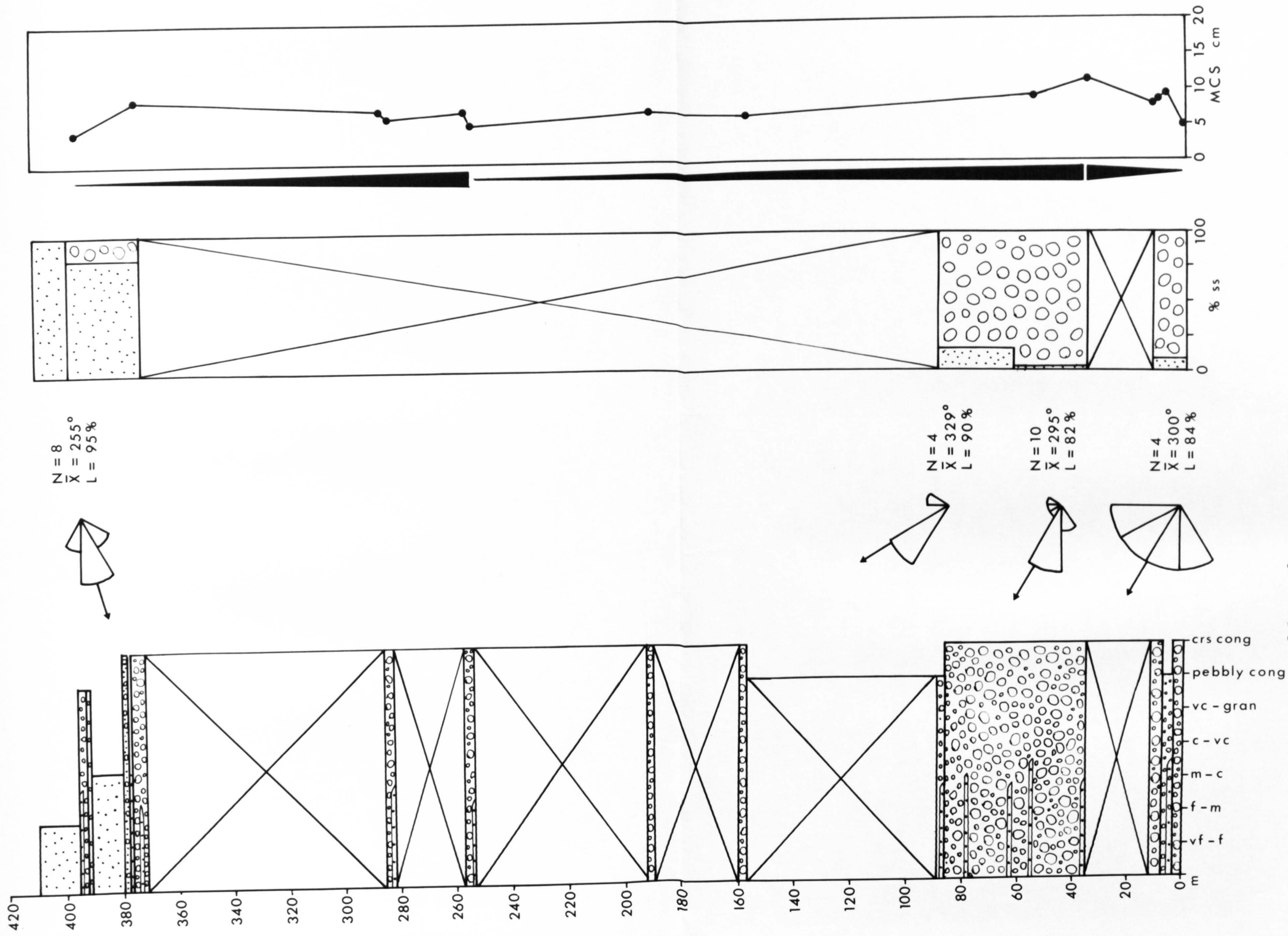
Straiton Section 2 Fig. 3-B



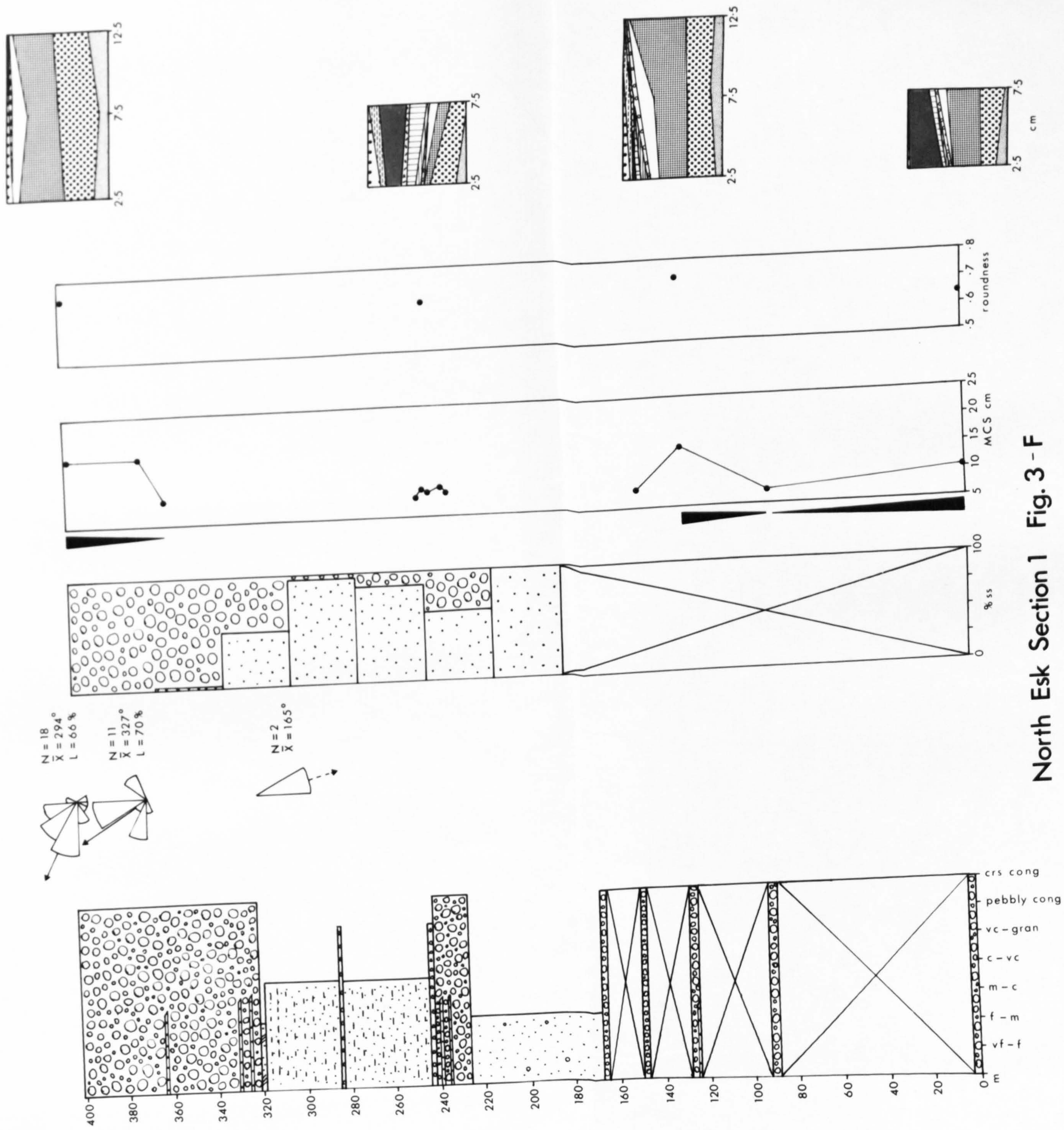
Hagshaw Hills Section 1 Fig. 3 - C



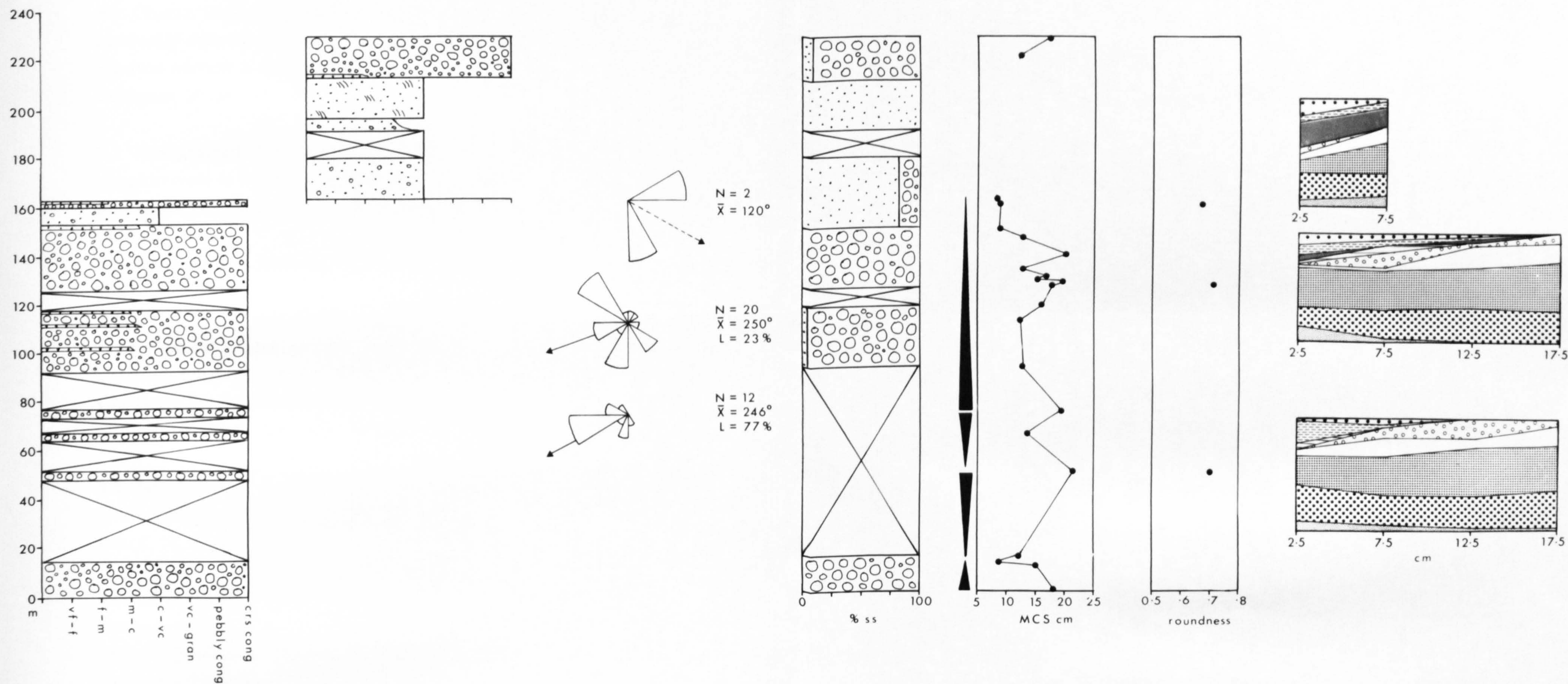
Hagshaw Hills Section 3 Fig. 3-D



Hagshaw Hills Section 5 Fig. 3-E



North Esk Section 1 Fig. 3 - F



North Esk Section 2 Fig.3-G

Plates

3.1 Non-repeating, medium-scale planar cross-bedding in sandstone facies sequence at base of conglomerate sequence. Stration section 2.
Hammer, 60 cm or 2 ft, for scale.

3.2 Coarse, unstratified, clast-supported Gm1 facies conglomerate with randomly orientated rounded to well rounded sandstone clasts.
Straiton section 3, Auchigairn Burn.
Compass, 20 cm, for scale.

3.3 Fine-grained, clast-suppoorted Gm1 facies conglomerate. The conglomerate is moderately sorted with calcite cement laterally grading into poorly sorted conglomerate with outsized clasts. Imbrication is poorly defined.
Straiton section 4, Auchingairn burn. Compass for scale.

3.4 Coarse, unstratified, clast-supported Gm1 facies conglomerate. The conglomerate grades upward into very thinly developed medium to coarse-grained sandstone. Imbrication is developed in isolated clusters. Clasts are very well-rounded.
Straiton section 2. Compass for scale

3.5 Sandy, thinly bedded, poorly-sorted Gm1 facies conglomerate.
Sraiton section 2.
Pencil, 14 cm, for scale.

3.6 View of thinly bedded, well imbricated coarse Gm2 facies conglomerates.
Ridge exposures on Doubty Hill, Stration section 3. View to north
Back pack for scale.

3.7 Close up of plate 3.6, below yellow flowers in top left corner. Note general decrease in roundness compared to Gm1 facies, plates 3.2 & 3.4.
View to north
Compass for scale.

3.8 Small isolated lense of sandstone with concave bottom and convex top. Note conglomerate thins over crest of sandstone and sandstone thins in direction of palaeoflow. Compass for scale.

3.9 Large scale planar cross-bedding in Gm1 facies conglomerate. Stration on Hadyard Hill. Hammer for scale.

3.10 Trough cross-bedded pebbly sandstones and conglomerates. View approximately to north. Ridge exposures on Doubty Hill, Straiton section 4. Pencil for scale.

Bedding plane

Gm1 facies

Gm1 facies

plate 3.1



plate 3.2

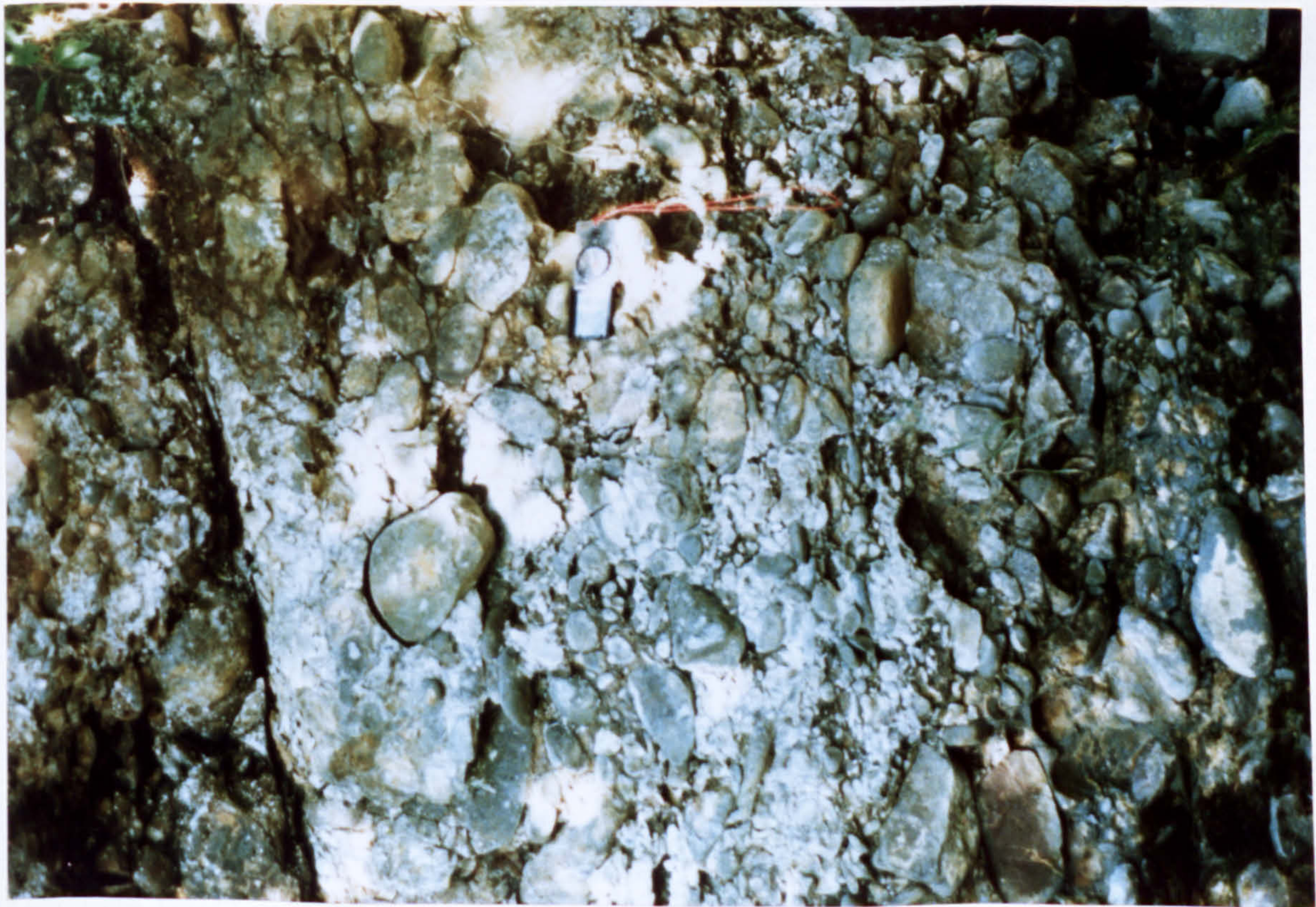


plate 3.1



plate 3.2



calcite[↑] cement

← isolated
imbricated clusters →

plate 3.3



plate 3.4



plate 3.3



plate 3.4



plate 3.5



plate 3.6



plate 3.7



plate 3.8



plate 3.9



plate 3.10



4.0 Petrography of the Greywacke Conglomerate sandstone clasts

Petrographic analysis was carried out on 196 samples of sandstone clasts from the Greywacke Conglomerate. All the petrographic results from the framework, granule and heavy mineral counts described below are given in Appendix A. The samples were mainly collected from the vertical sections described in Chapter 3, (see Figs. 3.1.7, 3.2.1, 3.3.2, 3.4.1). More than one sample was collected in each locality and in most localities 2-6 samples were collected. Samples near igneous intrusions were avoided. Statistical and conventional triangular plotting methods were used to ascertain lateral trends in the modal composition of the sandstones. Sandstone clasts taken from the Greywacke Conglomerate were also compared with published data from the Southern Uplands. However, operator error and bias can significantly effect the comparisons.

4.1 Counting techniques and descriptions of modal categories.

Approximately 400 grains were counted from each sample using an automatic point counter and the method described by Van Der Plas and Tobi (1965), where the point distance chosen is larger than the largest grain. The polymodal nature of many of the clasts requires a 0.7 mm point distance between grains. Using Van Der Plas and Tobi's chart for reliability (Van Der Plas and Tobi, fig. 1) a count of 400 grains per thin section would lead to a 2 sigma not greater than 5% at 95% confidence interval for a mineral content estimated between 2% and 98%. A count of 1000 grains per thin section would only decrease 2 sigma to 2%-3.2% for a mineral estimated between 10% and 90% by volume. It was therefore assumed that such a small reduction in the reliability of the mineral content (2 sigma) could not justify the exponential increase in point counting time for 1000 grains per thin section and a 400 grain count would produce a similar measure of reliability. In total, 173 samples from all the areas were used to form the framework grain count data matrix.

4.1.1 Framework grains, matrix, and cement.

Ten distinct modal categories were used and account for the majority of observable minerals within each thin section. The categories are: i). quartz, ii). feldspar, iii). basic igneous fragments, iv). acidic igneous fragments, v). metamorphic fragments, vi). sedimentary fragments, vii). altered grains and fragments, viii). cement, ix). matrix and, x). accessories. Within each group a number of subgroups can be identified.

a. Quartz. Quartz was divided into monocrystalline quartz, polycrystalline quartz and chert. Monocrystalline quartz is taken as a single quartz crystal or grain whereas polycrystalline quartz is taken as two or more quartz crystal aggregates. These two subgroups account for the majority of grains encountered in the clasts. Chert fragments are rare in the sandstones. Differentiation between fine-grained acidic fragments and chert can be a source of

error but many of the chert fragments have a slight hematite stain which is not developed in the acidic fragments. Relict radiolarian tests were seen in only one chert fragment. Rare chalcedony fragments were counted with chert fragments, however they may be products of devitrified volcanic glass.

b. Feldspar. Staining for feldspar was not undertaken due to the presence of many very small feldspars which when stained tended to obscure the matrix. The subcategories recognized in the feldspar group are twinned feldspar, untwinned feldspar, microcline-perthite, and carbonate altered feldspar (if relict feldspar still obvious). Large crystals of intergrown quartz and feldspar were counted with the respective host the cross hair fell upon.

c. Basic igneous fragments. Fine-grained basic igneous fragments were not divided into separate classes due to the extensive alteration usually associated with these fragments. However, this alteration was used for distinguishing between the basic and more acidic fine-grained igneous fragments. A high proportion of chlorite and/or oxide alteration as well as abundant lath shaped feldspars in the fragments were characteristics used to differentiate basic from acidic igneous fragments.

d. Acidic igneous fragments. A variety of acid fragments can be recognized mainly on textural criteria. Felsite fragments, usually composed of a microcrystalline mosaic of feldspar and quartz with or without phenocrysts of quartz and/or feldspar, are very common in the more volcanic rich sandstones. Rhyolitic fragments are cryptocrystalline and generally have phenocrysts of quartz. Dickinson (1970) has described a microlitic type of volcanic fragment which has euhedral feldspar prisms in a felted or trachytic texture or alternatively hyalopilitic patterns of microlites and suggests that these fragments are mainly the products of intermediate volcanics. These texture have also been recognized but are consistently very clean with very little chlorite or oxide alteration and thus have been classified as acid fragments. Another unique type of fragment, 'coarse felsitic', is seen where relatively large crystals of sutured and wavy feldspar form a mosaic pattern with occasional laths of feldspar contained in the felsitic mosaic. These fragments probably represent products of devitrified acidic volcanic glass. Microgranite, sometimes with granophyric texture, and coarser fragments of quartz and feldspar occur in a minority of sandstone clasts.

e. Metamorphic fragments. Fragments include phyllites and grits, schist/gneiss and metaquartzites. Phyllites are very fine grained fragments usually quite dark with a chlorite and white mica cleavage. Grits resemble the sandstones being studied but banding produced by pressure solution has replaced original grain boundaries and cleavage parallel to these bands is developed. In both, the phyllites and grits original detrital grain boundaries can still be seen in some areas. Neither of these fragments are ever abundant.

Schist fragments are very common and are typically qtz-muscovite schist, qtz-chlorite-muscovite schist, or qtz-feldspar-mica schist. Biotite schists are very rare. The majority of schists are fine-grained and very small acicular rutile is a common constituent. A number of these fragments have crenulated cleavage and superimposed on the cleavage is randomly oriented mica. Medium-grained schist/gneiss show both feldspar and quartz banding with muscovite and chlorite being the dominant mica. Euhedral apatite parallel to cleavage and rare euhedral tourmaline randomly oriented occur in the schist/gneiss group.

Metaquartzites are also a very common subgroup. This subgroup can be distinguished from polycrystalline quartz if: i) they contain oriented mica, ii) crystals are stretched with sutured boundaries or iii) have a number of very small crystals typically occurring with larger crystals (Blatt, Middleton, and Murray, 1980). Feldspathic quartzites are common and aid in the identification of metaquartzites. The feldspars usually contain abundant inclusions of quartz.

f. Sedimentary fragments. Sedimentary fragments are infrequent in the sandstone clasts. Fragments include shale, siltstone and sandstone clasts. Sandstone clasts are either well-sorted, well-rounded, quartz rich sandstones or poorly-sorted matrix rich sandstones which are only discernable from the host sandstone by a difference in grain size.

g. Matrix. Matrix was defined as anything less than 0.03mm. At this grain size the matrix is composed of quartz, feldspar, with much of the material composed of chlorite and white mica. X-ray diffractions of material less than 0.5-1.0 μ from sample 16h1 (Fig. 4.1.1), but representative of the conglomerate as a whole, show that true clay particles (e.g. illite, montmorillonite) were not present in any quantity and instead chlorite, muscovite, quartz, feldspar as well as a minor amount of calcite occur in the less than 2 μ fraction with an increase in quartz and feldspar in the 2-5 μ fraction.

h. Altered grains and fragments. This category contains all the grains and fragments which have been altered beyond recognition. Four main subgroups occur sericite, calcite, oxide, and chlorite. Feldspar alters to both calcite and sericite and it is probable that the first two subgroups represents a high proportion of altered feldspar. The last two subgroups is most likely to be alteration products of mafic minerals or fragments.

i. Cement and veins. Replacement calcite occurs as finely disseminated crystals of calcite and syntaxial replacement of whole detrital grains. Syntaxial pore filling cement is not a feature of these sandstones. Carbonate replacement can be extensive in some samples with only silica rich fragments surviving, even these showing attack along the grain

boundaries. Oxide-Cement occurs as patches of microcrystalline cement irregularly surrounding detrital grains. Detrital grains adjacent to these patches show a high amount of replacement by finely disseminated oxide crystals. Hematite and Limonite account for the majority of oxide cement associated with the sandstones.

Two types of veins are recognized; calcite and silica. Both minerals can exist together in the same vein, quartz typically surrounding and being secondary to calcite. Quartz veining shows a gradation from clear quartz with straight boundaries outward to areas within the sandstone with extensive pressure solution and total loss of grain boundaries. Psuedo-quartz veins, patches of quartz rich areas with complete loss of grain boundaries, occur sporadically in quartz rich sandstones. Psuedo veins are not counted with the the silica-vein but instead counted as mono quartz, even though polycrystalline quartz may be represented.

j. Accessories. Four subcategories of accessories are recognized: i). opaques, ii). micas, iii). epidote and, iv). others which make up the remainder of constituents in the sandstones. Opaques are dominately large rounded grains of hematite with minor amounts of other detrital opaques. Muscovite is the most common mica accessory with chloritized biotite and chlorite forming only a small percentage of this subgroup. Epidotzite is counted with single grains of epidote in the heavy mineral count. Associated with large amounts of accessory epidote in individual samples is abundant fine crystalline thought to be authogenic epidote. These fine-grained epidotes are also counted with the heavy minerals since it is unclear if all are truly authogenic. Tourmaline, Rutile, Garnet, Sphene, Zircon and Apatite are the remaining accessory minerals within the "other" subgroup.

4.1.2. Granule counts.

23 samples from the Straiton, Hagshaw Hills, and North Esk areas were used to delineate the modal abundances of granules, minerals and fragments ≥ 1 mm, in the respective regions. Eight separate categories were defined using the same criteria as in sect. 4.1.1, framework grains. The eight categories are: i). quartz, ii). feldspar, iii). basic igneous rock fragments, iv). acidic igneous rock fragments, v). metamorphic rock fragments, vi). sedimentary rock fragments, vii). altered minerals and rock fragments and, viii). other. The minerals which form the "other" category are rare occurrences of large grains of muscovite and garnet. Using an automatic point counter the first 100 grains, ≥ 1 mm, seen along a systematic transect of each thin section were counted. In two cases, less than 100 grains, 93 and 99, were encountered.

4.1.3. Heavy minerals.

Heavy mineral separation was not carried out due to the degree of induration of the sandstones. Instead, each occurrence of Epidote, Tourmaline, Rutile, Garnet, Sphene, Zircon, Apatite, and Quartz containing vermicular chlorite encountered during the point count transect across the thin section was noted. This data does not represent an accurate count of every grain in the thin section but relative abundance can be ascertained. A total of 158 samples used in the framework grain count included heavy mineral counts. Heavy mineral counts were not carried out on the samples used for granule counts.

4.2. Texture and diagenesis of the Greywacke Conglomerate Clasts.

Greywackes were defined as a field term to describe well indurated, dark, grey-green, sandy members of rhythmically thin inter-bedded sand shale sequences (Blatt *et al.* 1980). The arenaceous units are commonly fine-medium grained and resemble in hand specimen hypabyssal basic igneous rocks. The beds are typically unstratified, however graded bedding is common. Cross-bedding when present is confined to very small scale features, less than 7 cm. Today, these features are associated with deposition of turbidites.

The above field description accurately describes in hand sample the sandstone clasts seen in the Greywacke Conglomerate but many of the clasts have been stained red obscuring the original colour. Very small scale low-angle cross-bedding and graded bedding occur but are rare features of the clasts.

In thin section, greywackes are defined either on the basis of texture, an immature sandstone containing > 15% matrix, or composition, a sandstone which has a higher proportion of unstable lithic fragments compared to feldspars (Dickinson, 1970). Texture is generally considered to be the more definitive criteria for applying the term greywacke to a sandstone.

The texture of the clasts in thin section is unique for each sample but a general account of the common features is given. Typical thin sections from each area are shown in plates (4.1-4.5). The samples range from poorly to moderately-sorted, fine to granule sized sandstones. The average matrix in each area varies from 8.9% to 16.6% (Table 4.3.1). Using the classification from Pettijohn *et al.* (1972, Fig. 5-3), based on the percent matrix, > 15% matrix for wackes and < 15% matrix for arenites, the Straiton and Hagshaw Hills samples are classified as lithic arenites whereas the Carmichael and North Esk are feldspathic arenites and the Tinto samples are classified as feldspathic wackes.

The majority of the samples are poorly-sorted and polymodal. The degree of rounding varies with varying size and mineralogy as well as between different areas and a more complete account is given in section 4.3.1. Orientation of the angular grains and elongated minerals along bedding is rare in the poorly-sorted varieties. Bedding is more commonly seen in the moderately-sorted, quartz-rich, matrix-poor samples indicating selective sorting during transportation of these samples.

The percentage of matrix generally increases with increasing grain size and degree of alteration and suggests that at least part of the matrix is diagenetic. Corrosion along framework grains and replacement by finely crystalline chlorite and sericite confirms the presence of diagenetic matrix. Microcrystalline quartz and feldspar are common as matrix constituents particularly in severely sheared areas of the thin section.

Some degree of alteration and diagenesis is found in all the areas and varies with mineralogy and texture. Compaction features, squeezed soft rock fragments (sedimentary fragments, phyllites and schists) and bent micas are often seen in the poorly sorted varieties. Severe loss of grain boundaries forming concavo-convex boundaries are favoured in quartz-rich sandstones.

Quartz and calcite veins along with small scale shear zones occur in the samples. It is difficult to know precisely if these features are associated with post or pre-deposition of the clasts in the Greywacke Conglomerate. At least some of the veins and fracture are post-depositional and associated with faulting in the Greywacke Conglomerate. Finely disseminated authogenic epidote is found in the Tinto, Carmichael, and North Esk samples where detrital epidote is common. The authogenic crystallization of epidote may have been precipitated by the increased heat from felsite intrusions in these areas. The sheared zone boundaries in the sandstone clasts are occasionally confined to areas within the thin section and indicate that they are deformational features within the original sediment.

As noted earlier replacement of the original rock by carbonate can range from single grain pseudomorphs to extensive replacement with only the quartz-rich fragments remaining. Again, it is difficult to know how much replacement is post-or pre-deposition of the Greywacke Conglomerate. Calcite veins (greater than 30 cm wide) which cut the Greywacke Conglomerate indicate considerable introduction of carbonate rich fluids after deposition of the Greywacke Conglomerate.

Hematite staining is common and introduced after deposition of the clasts into the Greywacke Conglomerate. Clasts and matrix within the Greywacke Conglomerate range

from red to grey-green from outcrop to outcrop. Single clasts can show a variation in colour from half red to half green suggesting fluid migration and oxidation-reduction fronts within the Greywacke Conglomerate.

4.3 Analysis of petrographic data.

Table 4.3.1 lists the average modal abundances of each category for the different regions of the Greywacke Conglomerate along with their respective subcategories, recorded as a percentage of each category, described in section 4.1.1. This data was used to build a series of triangular plots to compare the variation in mineralogy within and between the Greywacke Conglomerate (sect. 4.3.1). A similar set of triangular diagrams are used for comparison with published data for the Southern Uplands sediment in section 4.3.2. The modal abundances for the respective three apexes on each triangular diagram were recalculated to a percentage of the sum, 100%, of the three primary parameters. In addition to the above conventional triangular diagrams, Q-mode factor analysis on the Midland Valley clasts and Southern Uplands sediments, and cluster analysis on the heavy mineral counts from the Midland Valley clasts, were employed. The results of the petrographic analysis can then be used to describe the source region which supplied the sediment, the geotectonic framework of the source region, and the similarity of the source region to the Southern Uplands.

4.3.1. Trends within the Midland Valley Greywacke Conglomerate clasts.

a). Framework Grains. In Figs. 4.3.(1-4) a series of triangular plots define the major mineral constituents in each area. The graphical parameters are self-explanatory except (a.) which follows the parameters used by Walton (1955) where Q=quartz + siliceous fragments including acidic igneous fragments, chert and metamorphic fragments, F=feldspar + basic igneous fragments and M=matrix + sedimentary fragments.

In the Straiton area the samples are characterized by a high percentage of quartz and siliceous fragments. Chert, sedimentary and basic igneous fragments are essentially zero, thus the parameters in Fig. (4.3.1 a) effectively measure only matrix, siliceous fragments and feldspar. Feldspar is typically less than matrix and along with the high percentage of siliceous fragments the Straiton sandstones are a compositionally mature suite of sandstones. Texturally, the relatively high proportion of matrix places the sandstones into a texturally immature category however a few samples are both texturally and compositionally mature sandstones. Metamorphic rock fragments form over 80% of the total rock fragments recorded in the majority of these samples (Fig. 4.3.1 b). A comparison between Fig. (4.3.1 c and d) shows a significant proportion of the total quartz is polycrystalline quartz (c. 25% on average).

Though there is some degree of overlap a clear separation in the mineralogical content of samples from section 1 and section 2 is seen in the diagrams. The samples from section 1 are depleted in feldspar and have higher amounts of mono- and polycrystalline quartz. Higher amounts of acidic and basic volcanics are found in section 2 whereas the rocks fragments from section 1 are almost solely derived from metamorphic rocks.

In the Straiton area the largest grains are mono-polycrystalline quartz and metaquartzite. The quartz grains and fragments are typically angular and show strongly undulose extinction.

Fine-grained low-grade schists and phyllites are frequently rounded and smaller than quartz-rich metamorphic fragments, the difference in roundness here is probably a function of the degree of hardness rather than distance from the source. However, well rounded broken metaquartzites suggest polycyclic or a long history of transportation for some of these fragments. Metamorphic fragments show a complete gradation from phyllites and grits to high-grade gneisses and feldspathic quartzites. The feldspars in the metaquartzites are strained and contain bled-like inclusions of quartz. Low-grade feldspathic schists have numerous orbital and wavy needle-like inclusions of rutile grown during metamorphism (plate 4.6). These inclusions, rutile and quartz, are frequently associated with single grains of feldspar implying that much of the feldspar is derived from metamorphic rocks. Rutile needles are also abundant along the cleavage planes of muscovite schists.

Acidic and basic igneous fragments are typically better rounded than quartz of equivalent size. The acidic fragments in contrast to the basic fragments can occur in the largest size fraction of the sample particularly in section 2. Embayed quartz is present within the acidic volcanic fragments and only rarely seen as detrital grains. Subhedral and euhedral laths of feldspar are absent from all the samples and the twinned feldspars show some degree of rounding. The presence of metaarkoses (although rare) indicates that some of the twinned feldspar could be derived from metasediments. The volcanic fragments show a history of deformation prior to deposition in the sandstones and include veined acidic and basic fragments and deformed acidic fragments with cleavage development, (plates 4.7-4.8).

The Hagshaw Hills samples are compositionally less mature than the Straiton samples with a decrease in stable siliceous fragments accompanied by an increase in feldspar and basic igneous fragments. Matrix percentages do not show any considerable variation within the sandstones but are higher than the Straiton samples and an overall decrease in compositional and textural maturity is indicated (Fig. 4.3.2 a). A significant proportion of the total quartz is polycrystalline and the samples mineralogically resemble the samples

from Straiton section 2 in percent mono- polycrystalline quartz, total rock fragments and feldspar (Fig. 4.3.2 c-d). However, there is a shift toward decreasing metamorphic fragments and increasing volcanic rock fragments, specifically acidic volcanics, (Fig. 4.3.2 b). There is no overall mineralogical difference between the different sections in the Hagshaw Hills area but there is considerable variation in the percentage of different rock fragments within the Hagshaw Hill samples. The percentage of metamorphic fragments in a number of these samples is as high as that obtained in the Straiton samples.

Monocrystalline quartz is the most frequent modal class in the largest size fraction but also includes a high percentage of acidic volcanics. Large untwinned feldspar grains, sedimentary sandstones, and fine-grained metamorphic fragments are more common than in the Straiton sandstones.

The metamorphic rock fragments in many ways resemble the Straiton sandstones with a range of metamorphic fragments from low-grade to high-grade fragments common. However, untwinned feldspar with inclusions of quartz and rutile are less frequent and low-grade phyllites and grits are more frequent.

Basic igneous rock fragments show the highest degree of roundness of the rock fragments and are on average smaller in grain size, a feature consistent with the Straiton samples. Acid volcanic fragments range from rounded to angular, of the two angular fragments are more common. A wide variety of textures is seen in both the volcanic classes in any one sandstone. Euhedral and subhedral laths of feldspar are not observed and twinned feldspar is subordinant in both size and frequency to untwinned perthitic feldspar.

Samples from the Tinto and Carmichael regions are compositionally mature sandstones with a high proportion of siliceous minerals and fragments (Fig. 4.3.3 a). The majority of these samples are finer-grained than in the other areas and higher percentages of monocrystalline quartz would be expected. High amounts of polycrystalline quartz are however still found in these sandstones (Fig. 4.3.3 c-d). Compared to the Hagshaw Hills there is an increase in total feldspar. In the majority of these samples total feldspar is less than total rock fragments but high values of feldspar with correspondingly low values of total rock fragments and total quartz shift the average toward feldspathic wackes. Many of these samples are thus lithic wackes with high feldspar contents.

There is a wide variation in rock fragments similar to the Hagshaw Hills samples, particularly in the Carmichael samples which range from 100% metamorphic fragments to 100% volcanic fragments, (Fig. 4.3.3 b). Compared to the Hagshaw Hills samples higher percentages of basic volcanics rock fragments and lower percentages of acidic volcanic

fragments are found. Metamorphic rock fragments are still the dominant rock fragment. There is no significant difference in the overall mineralogy between the Tinto and Carmichael samples.

Angular monocrystalline quartz is the most frequent modal class at all size fractions. Large often rounded detrital perthite is common, particularly in the Carmichael area and correlates with an increase in large rounded-subrounded microcline. The largest fragments also include angular-rounded basic, intermediate and acidic igneous rock fragments.

The first appearance of biotite-rich intermediate volcanics (plate 4.3) is seen in these samples and correspond to an increase in detrital biotite. Veined basic volcanics have also been noted. Granitic fragments, although rare, could be a possible source for some of the perthitic feldspar. Much of the feldspar, twinned and untwinned, is derived from both plutonic and volcanic fragments. Clear subhedral rounded and embayed quartz is more frequent in these sandstones compared with the previous areas. Metamorphic fragments include all the varieties noted before but are typically smaller in grain size. Although feldspar-rich metamorphics are commonly encountered, detrital feldspar with inclusions of quartz and rutile are less frequent than in either the Straiton or the Hagshaw Hills samples.

Epidote-altered detrital feldspar and epidote altered acidic-igneous fragments are associated with abundant detrital epidote (plate 4.4) indicating that much of the epidote is derived from metamorphosed igneous rocks. Well rounded detrital tourmaline with secondary euhedral overgrowths confirm the presence of metasedimentary material in the source region (plate 4.9).

The North Esk samples are similar to the Tinto-Carmichael samples in compositional maturity with a proportionately high percentage of siliceous fragments (Fig. 4.3.4 a). Feldspar exceeds total rock fragments in the majority of the samples but, however, large percentages of polycrystalline quartz are still recorded from these rocks (Fig. 4.3.4 c-d). Similar to the other areas metamorphic rock fragments are the most abundant fragments, with the exception of the samples from section 3 which have very high percentages of acidic volcanic fragments (Fig. 4.3.4 b). The largest percentages of basic volcanic fragments are recorded from the North Esk sandstones but acidic volcanic fragments exceed basic volcanic fragments in the majority of the sandstones.

Samples from sections 1, 2, and 4 show a low variation in the overall mineralogical content and group in a tight cluster. Samples from section 3 have lower total quartz and metamorphic fragments and higher feldspar and acidic volcanic fragments. In contrast, samples from section 5 are compositionally the most mature sandstones in the North Esk with

higher percentages of metamorphic rock fragments and quartz.

Clear monocrystalline angular quartz is the most frequently occurring framework grain in the sand sized fraction. A high percentage of these quartz grains are subhedral with embayed and resorbed boundaries derived from acidic volcanic rocks. Accordingly, large rhyolitic and felsitic fragments are typical of the the North Esk sandstones. Basic volcanics are on average slightly smaller and more abraded than the acidic volcanic fragments. Biotite-rich volcanic fragments along with detrital biotite occur in these sandstones but with less frequency than in the Tinto-Carmichael region. Untwinned feldspar and perthite are more abundant than multiple twinned plagioclase and most of the feldspar resembles the relatively large feldspar phenocrysts in the acid volcanic fragments. Metamorphic fragments, although the dominant rock fragment are also the smallest rock fragments.

b). Granules. Rock fragments are size dependent and decreasing grain size gives rise to increasing monocrystalline quartz (Pettijohn, 1975). The degree of sorting in the sandstones and decomposition of rock fragments during transportation can adversely effect the conclusions about the relative abundance of source material gained from the finer-grained sandstones. Coarse-grained sediments can therefore be more representative with respect to the frequency and variety of rock fragments. Coarse-grained samples from the Tinto-Carmichael regions were not collected and are absent from the granule studies.

Sedimentary rock fragments make up only a small percentage of the total rock fragments from the majority of the granule-sized sandstones, (Fig. 4.3.5 a), samples from the Hagshaw Hills having the highest percentage of sedimentary fragments. There is only a very small increase in the number of volcanic fragments in the very coarse-grained sandstones compared to the finer-grained sandstones in the Straiton area, where at all sizes metamorphic fragments tend toward 100% of the rock fragments. The Hagshaw Hills and the North Esk both show a significant increase in the number of volcanic fragments in the granule-sized fraction compared to the sand-sized fraction. This increase is particularly high in the North Esk where volcanic fragments tend toward 100%. The volcanic fragments are dominately acidic in all areas, (Fig. 4.3.5 b), basic volcanics exceeding acidic fragments only in the North Esk samples.

In summary, lateral trends in the framework mineralogy can be seen in the Greywacke Conglomerate sandstone clasts reflecting a change in source rock composition. Comparison in the framework grains triangular plots from the Straiton (SW) samples to the North Esk (NE) samples shows a trend toward decreasing quartz and metamorphic fragments to increasing feldspar and volcanic fragments.

The Straiton samples are almost solely derived from a metamorphic source with very minor amounts of acidic volcanics exposed in the source region. The samples from Straiton section 1 are almost completely devoid of volcanics and exceptionally rich in clean metaquartz-arenites. The samples from section 2 have feldspar percentages similar to that seen in the Hagshaw Hills. The feldspars from the section 2 samples have abundant inclusions of quartz and rutile and are K-feldspars derived from metamorphic quartzo-feldspathic rocks. Drainage of a more diverse metamorphic region for the Straiton section 2 samples is seen, a low to high grade assemblage of feldspar-rich pelitic and psammitic schists and gneisses. The acidic volcanic fragments show signs of deformation and the source region may have included minor amounts of metavolcanics.

Drainage of a metamorphic source is indicated in all the samples. Decreasing importance of the metamorphic source and a concomitant increase in volcanic activity is seen from the Hagshaw Hills samples to the North Esk samples. The framework and granule studies suggest the Hagshaw Hills samples are strongly mixed sediments with almost equal proportions of metamorphic and acidic volcanic sources. The North Esk samples in contrast are volcanic rich with a high percentage of mature, acid, volcanic detritus. In the Hagshaw Hills and the North Esk basic volcanics are in general better rounded and smaller in grain size than acidic volcanics. The source for these basic volcanics probably lay some distance from the basin of deposition.

The samples from the Tinto and Carmichael areas resemble the North Esk in most aspects although there is a larger variation in compositional maturity with the most immature samples recorded from these areas. There is some indication to suggest equivalent proximal sandstones, the very coarse-grained sandstones, would be very rich in basic volcanics. Granitic detritus occurs more frequently in the Carmichael samples than in the remaining areas. It may be that plutonics were very localized in the source region or the Carmichael samples are either older or younger than the sandstones from the other areas.

c). Heavy minerals. Cluster analysis on 80 randomly selected samples with heavy mineral data was used to show the similarity of the heavy mineral populations from the different regions in the Greywacke Conglomerate. The heavy mineral data was coded according to the relative abundance of a particular mineral, similar to the method described by Till (1974). The code given for each mineral species is:

1= present or "no data", 0-5 occurrences

2=common, 5-15 occurrences

3=abundant, >15 occurrences

The coding system alleviates any problem associated with exceptionally high values of

epidote, where both authigenic and detrital minerals, are represented in the samples. Jaccard's coefficient of association was used to describe the degree of similarity between all pairs of samples and is defined as:

$$S_j = p / (p + m)$$

p=number of positive matches

(e.g. a matching of "1" with a "1")

m=number of mismatches

(e.g. a "1" with a "2" or "2"

with a "3" and so on)

The cluster dendrogram obtained is given in (Fig. 4.3.6). The vertical axis measures the degree of similarity between the samples with 0 representing complete dissimilarity and 1 complete similarity.

A clear grouping of the samples can be seen. The majority of Hagshaw Hills samples cluster with the Straiton samples in the heavy mineral category "Apatite-Zircon-Tourmaline-Garnet (rare)". Apatite, Zircon and Tourmaline are all particularly stable and suggest a certain amount of reworked sediment, originally derived from granitic detritus and latter metamorphosed, in the source region.

In contrast, the majority of the North Esk, Tinto, and Carmichael samples cluster in the "Epidote-Garnet-Sphene-Apatite" association. It has already been noted that epidote is a product of metamorphosed igneous rock fragments and feldspar. The common occurrence of epidote and garnet in these samples indicate that very little of the metamorphic source detritus for these minerals mixed with the Straiton and Hagshaw Hills samples possibly indicating a difference in age between the two groups. The metamorphic region for the garnets and the epidote (unless a product of hydrothermal alteration) was actively being eroded during original deposition of the T-C-NE sediments.

The samples between the two primary clusters show some degree of similarity to both clusters. Garnet and sphene present (epidote absent) in the Hagshaw Hills and Straiton samples and tourmaline and apatite more abundant in the North Esk samples (epidote present).

4.3.2. Comparison of the Midland Valley sandstone clasts and Southern Uplands greywacke sediments.

The Southern Uplands is comprised of a sequence of interbedded sandstones and shales separated by fault bounded blocks. The Southern Uplands can be subdivided into three major zones, the Northern, Central and Southern Belts. The boundary between the Northern and the Central Belts is defined as the boundary between the Ordovician rocks in the north and the first appearance of Silurian age rocks towards the south, (Fig. 1.1). In practice this boundary is commonly taken as the trace of the Kingledores Fault, however Llandovery age sediments may be present north of this fault. The southern boundary of the Central Belt is commonly taken as the Riccarton Line which separates mainly Llandovery age sediments in the Central Belt from mainly Wenlock age sediments in the Southern Belt.

A number of Groups and Formations are recognized in the Southern Uplands and poor exposure over much of the area prevents accurate correlations between the Groups and Formations to be made. Correlations that have been suggested are based mainly on compositional similarity of arenaceous sediments along strike within each belt. The compositional variation across strike shows an overall trend from mafic-rich sediments in the Northern Belt to progressively more siliceous sediments in the Central and Southern Belts. The various grains and rock fragments described from the sediments are similar throughout the Southern Uplands but the proportions may differ between the correlated units. The sediments from the Southern Uplands used for comparison to the Midland Valley clasts cover a large areal extent through most of the vertical section; tracts 1-10, tracts I-IV, (Fig. 4.3.7).

Northern Belt Greywackes (Tracts: I, II, and III)

The Northern Belt sediments are predominantly medium to coarse grained greywackes, Caradoc to (?)Ashgill in age, characterized by a repetition of quartz-poor and quartz-rich sandstones. Greywacke successions along the Rhinns of Galloway (Kelling, 1958; 1962) tracts I, II, and III show a compositional and lithologic similarity to greywackes across the Loch Ryan Fault (Welsh, 1964) and up to 80 km inland along strike in West Nithsdale (Floyd, 1982; 1975). The following correlations proposed by Floyd (1975) between the three areas are based mainly on compositional similarity.

Portpatrick (acid)-Boreland-Shinnel Formations. Relatively quartz-rich greywackes with detrital ferromagnesian (pyroxene and hornblende material). A variety of metamorphic fragments including, schists, quartzites and detrital garnet typical of the Shinnel Formation, are present in small quantities in all the formations. Acid-igneous fragments are abundant in the Shinnel and Portpatrick (Acid) sediments. The Boreland sediments are considerably more basic with feldspar > quartz and basic igneous fragments >

acid igneous fragments.

Portpatrick (basic)-Glenwhan "Rocks"-Scar Formation. Quartz-poor sandstones, feldspar > quartz, with abundant basic igneous rock fragments and detrital ferromagnesian minerals. Detrital glaucophane and glaucophane schists have been recorded from the Scar and Glenwhan sediments, respectively.

Corsewall-Glen App-Marchburn. Sandstones rich in a variety of coarse and fine-grained acidic and basic igneous rock fragments. Feldspar generally exceeds quartz but the distribution of ferromagnesian minerals is variable within the formations, the most basic sediments containing high amounts of fresh pyroxene and hornblende. Serpentinite has been recorded from the Marchburn Formation. Representative samples from the Glen App Formation were not used for comparison with the Midland Valley clasts.

Kirkcolumb-Lochryan-Afton. Quartz-rich, feldspar-poor sandstones with a relatively low percentage of igneous fragments. Detrital pyroxene and hornblende are relatively rare although basic igneous fragments typically exceed acid igneous fragments. Igneous fragments are subordinate to metamorphic fragments and within the Kirkcolumb Formation the Metaclast Division is particularly rich in metamorphic fragments including andalusite.

Galdenoch-Cairn Sean-Blackcraig. Quartz-poor, feldspar rich sandstones with a variety of fine and coarse-grained basic igneous fragments. The sandstones are relatively rich in detrital ferromagnesian minerals.

Central Belt Greywackes

Tracts: IV-V, 4-6

The Killfillan and Garheugh Formations studied by Gordon (1962) in the Glenluce area (tracts IV-V) are recognized as the type formations for the northernmost Silurian greywackes. The Killfillan Formation comprises relatively mature greywackes rich in quartz, feldspar < quartz, and acid igneous rock fragments. Orthoclase, microperthite, and granitic fragments are common. Although the sediments are rich in quartz, basic igneous fragments occur in significant amounts and include rare serpentinite. Pseudomorphs of chlorite after pyroxene and hornblende occur in small proportions but the sediments are devoid of fresh ferromagnesian minerals. Sedimentary fragments, including black shales and well rounded arkoses, exceed metamorphic fragments which are relatively rare.

Quartz and acid igneous fragments increase upward through the section in the Garheugh Formation. The sediments are depleted in basic igneous, sedimentary and metamorphic fragments. Feldspar proportions tend to equal that seen in the Garheugh Fm.

Greywackes in the Peebles area (tracts 4, 5, 6) have similar compositions to those in the Glenluce area and on this basis Walton (1983) has proposed that the 'Pyroxenous Group' can be correlated with the Killfillan Formation and the 'Intermediate Group' can be correlated with the Garheugh Formation.

In tract 6 the Birkhill Shales, the 'Moffat Shale Group', are overlain by the Gala Group Greywackes. The greywackes are highly siliceous with high percentages of polycrystalline quartz and acid-igneous and are regarded as the type locality of the 'Garnetiferous Group' of Walton (1955).

Between tracts 5 and 6 a group of sandstones, the Meggett-Manor sandstones form part of the Gala Group studied by Casey (1984) who concluded the sandstones, in general, resembled those of the 'Intermediate Group'. The sandstones are rich in quartz, intermediate and acid volcanics are common, and plagioclase exceeds untwinned feldspar (microcline and perthite rare).

Tract 8

Towards the southern margin of the Central Belt in tract 8 the Upper Ordovician Shales, the Hartfell Beds, conformably pass into the Llandoverly Birkhill Shales. Within the 'Moffat Shale Group' a relatively thick sequence of greywackes, the Upper Hartfell Beds, Ashgillian in age are found. The greywackes are texturally immature with a high percentage of matrix (avg. > 20%) but compositionally mature with a framework of well rounded monocrystalline quartz, Casey (*ibid*). Interbedded sandstones within the Lower Birkhill Shales are compositionally and texturally similar to the Ashgill age sandstones. Upward through tract 8 the Upper Birkhill Shales are overlain by the Abbotsford Flags which are similar to the 'Garnetiferous Group' greywackes but are richer in both quartz and feldspar and depleted in lithic fragments, Casey (1984, Fig. 4.3).

Siccar and St. Abbs Head

Along the Berwickshire Coast, near St. Abbs Head, the greywacke sequences can be equated to the 'Garnetiferous Group' greywackes of Walton (1955). The sandstones are quartz-rich but there is considerable compositional variation within the formations with high percentages of rock fragments and polycrystalline quartz in the Siccar Formation and high percentages of feldspar and volcanic rock fragments in the Westloch Formation, the Buskin Formation is intermediate between the two, Casey (1984, A 3.9-A 3.12).

Central and Southern Belts (Tracts: 9 and 10)

The Wenlock age rocks of the 'Hawick Rocks' and 'Riccarton Group' vary little in

composition. The sandstones are quartz-rich and acid igneous fragments are the dominant rock fragment. Orthoclase and plagioclase feldspar along with basic igneous fragments occur in equal but small proportions, Warren (1963). Carbonate replacement is extensive and much of the carbonate has been recorded as matrix by Warren (*ibid*).

The mean modal composition from the above sandstone 'Groups' and Formations were calculated and used for comparison with the Greywacke Conglomerate. Very few of the samples from the Straiton and Hagshaw Hills areas have modal abundances comparable to the formation means in the Southern Uplands Ordovician sediments (Fig. 4.3.8). However, there is a greater similarity between clasts from the Tinto-Carmichael and North Esk areas and the Ordovician sediments. The similarity is particularly strong with the Shinnel Formation but 'equivalent' formations toward the southwest, the Boreland and Portpatrick (acid) have a higher percentage of mafic detritus. A few samples from the Tinto-Carmichael region do have high mafic percentages consistent with sediments from the Boreland and Portpatrick(acid) however the majority of samples are more siliceous and compare more closely to the Shinnel Formation.

The Tinto-Carmichael and North Esk samples also show some similarity to the Kirkcolm-Loch Ryan-Afton sediments but again these latter sediments are not only more mafic but also have higher amounts of matrix.

The Shinnel Formation has a similar composition to the Afton-Kirkcolm-Loch Ryan sandstones and a mixed acid igneous and metamorphic terrain has been postulated as the source region for all these sediments, (Floyd, 1975; Kelling, 1962; Welsh,1964). A similar source region has been suggested in this study for the Tinto-Carmichael and North Esk sandstones. However, metamorphic fragments are more common in the Midland Valley sediments than in the Ordovician of the Southern Uplands, where both acid and basic igneous fragments are common.

Using data from Floyd (1975) and Kelling (1962) a comparison between the granules, mean modal % rock fragments ≥ 1 mm, in the Southern Uplands sediments, and coarse to very coarse-grained samples from the Greywacke Conglomerate is shown in Fig. (4.3.9). The Ordovician sediments are enriched in sedimentary and volcanic fragments and depleted in metamorphic fragments compared to the Midland Valley clasts, (Fig. 4.3.9 a), a situation similar to the finer grained sandstones. Again, it is only the most siliceous formations from the Ordovician sediments which have similar proportions of metamorphic, acid volcanic, and basic volcanic fragments to samples from the Hagshaw Hills and North Esk regions, (Fig. 4.3.9 b). The North Esk is the only region to contain clasts which have extremely high

proportions of volcanic fragments, approaching 100%, comparable to the Ordovician sediments. Although, the volcanic fragments from the North Esk are almost exclusively acidic whereas the Ordovician sediments have higher percentages of basic fragments.

A comparison of the Midland Valley clasts with the mean modal compositions from the Silurian sandstones is shown in Fig. (4.3.10). The 'Garnetiferous and Riccarton Groups' are the most siliceous sediments in the Southern Uplands. These sediments are very low in feldspar and this coupled with the high percentage of quartz and quartz-rich fragments leads to a compositional similarity with the Straiton section 1 samples, (Fig. 4.3.10 a). Although there is considerable compositional similarity, the Straiton samples have a high percentage of low-grade metamorphic fragments and metaquartzites which was not recorded by Warren (1963) and virtually no garnets typical of the 'Garnetiferous Group', Walton, (1955). The samples from Straiton section 2 compare with the most siliceous sediments from the 'Intermediate Group' however the Straiton samples have on average higher proportions of metamorphic fragments and feldspar and less acidic igneous rock fragments.

The Hagshaw Hills, Tinto-Carmichael, and North Esk samples have an overall compositional maturity indistinguishable from the Garheugh and 'Intermediate Group' sediments, (Fig. 4.3.10 b-d). The Hagshaw Hills samples are similar to both the 'Intermediate Group' and the Garheugh Formation while the Tinto-Carmichael and North Esk samples show a stronger similarity to the Garheugh Formation.

In Figs. (4.3.11 a-b) 30 randomly selected samples from the Midland Valley, 20 randomly selected samples from the Glenluce (Gordon, 1962), Killfillan-Garheugh Formations, were plotted along with the mean modal compositions from the sediments in tracts 8, between tracts 4-5, and St. Abbs Head (Casey, 1984). Fig. (4.3.11 c) plots the mean modal compositions from the Central Belt greywackes given in Casey (*ibid*) along with the randomly selected clasts from the Midland Valley. The Silurian sediments have very little metamorphic detritus and high proportions of volcanic detritus, predominately acidic, with a significant percentage of sedimentary material, (Fig. 4.3.11 a). In contrast, the Midland Valley clasts have virtually no sedimentary detritus and volcanic detritus is subordinate to metamorphic material.

The sandstones within tract 8, the Ashgill greywackes and the Birkhill Grits, are exceptionally rich in total quartz and low in rock fragments and feldspar and thus have no similarity to the Midland Valley clasts, (Fig. 4.3.11 b). The 'Garnetiferous Group' greywackes and its 'equivalents', the Abbotsford Flags and the Siccar-St. Abbs Head sandstones, are richer in total quartz than the majority of the Midland Valley sandstones and compare only with total quartz from samples in Straiton Section 1. There is considerable

variation in the 'Garnetiferous Group-equivalent' greywackes. The Abbotsford Flags are depleted in polycrystalline quartz whereas the Straiton Section 1 samples are rich in polycrystalline quartz. Although the 'Garnetiferous Group' are rich in polycrystalline quartz both the 'Garnetiferous Group' and the Siccar-St-Abbs Head sandstones have less total quartz than the Straiton Section 1 samples.

The Midland Valley sandstone clasts have higher percentages of feldspar and a higher ratio of polycrystalline quartz/monocrystalline quartz compared to the Intermediate-Garheugh-Meggett Manor sediments, (Fig. 4.3.11 b-c). Unlike the Midland Valley clasts, the 'Pyroxenous Group'- Killfillan Fm. sandstones are exceptionally rich in rock fragments, mainly basic and acid volcanics, and depleted in both mono- and polycrystalline quartz.

There is also a difference in the proportions of different rock fragments found in the coarser grained sediments from the Midland Valley clasts and the Garheugh-Killfillan sediments. The Garheugh-Killfillan sediments both have higher proportions of sedimentary rock fragments and a lower occurrence of metamorphic detritus, (Fig. 4.3.12 a). The percentage of acidic volcanics to basic volcanics in the Silurian sediments is similar to that in the volcanic rich clasts from the Midland Valley, particularly in the North Esk samples, however, the variation in the proportion of metamorphic to volcanic fragments is widespread in both the Hagshaw Hills and North Esk samples and low in the Silurian sediments, (Fig. 4.3.12 b).

In summary, the compositional maturity of the Silurian Garheugh-'Intermediate Group'-equivalent sandstones is very similar to the Midland Valley sediments but the two groups shows significant differences in overall mineralogy. This mineralogical difference and similarity in compositional maturity is easily explained, the higher proportion of polycrystalline quartz and metamorphic fragments in the Midland Valley clasts offsets the effects of higher acid volcanics in the Silurian sandstones and similarly the higher percentages of feldspar in the Midland Valley clasts offsets the effects of higher basic igneous fragments in the Silurian sandstones.

4.4 Q-mode Factor Analysis.

The primary purpose in Q-mode Factor Analysis is to identify end members having extreme properties, in this study, the proportions of the major minerals and rock fragments. Objects or samples can then be classified and grouped according to their position relative to the end members.

In Q-mode Factor Analysis the interrelationship between samples are analysed. The degree of similarity between two objects from the original $(n \times p)$ data matrix, where n

represents the samples (rows) and p the variables (columns), can be measured using a coefficient of similarity analogous to the correlation coefficient. To measure the degree of mineralogical similarity between the Southern Uplands sediments and the Midland Valley clasts the $\cos \theta$ similarity coefficient, (Imbrie and Van Andel, 1964) was used. Before calculating the similarity matrix the original data matrix was transformed so each variable was expressed as a percentage of its range. This was done in order to give equal weight to each variable. The $\cos \theta$ similarity coefficient is defined as:

$$\cos \theta = \frac{\sum_{j=1}^p x_{nj}x_{mj}}{\sqrt{\sum_{j=1}^p x_{nj}^2 \sum_{j=1}^p x_{mj}^2}}$$

n, m= any two rows in
original (n x p) matrix

or in matrix notation: $W=D^{-1/2}X$
 $H=Wt(W)$

t=transpose
X=original data matrix
D= diag(Xt(X))

The $\cos \theta$ is an angular measurement of similarity ranging from 0 (vectors at 90°) to 1 (collinear vectors).

The similarity or association matrix, H, obtained is then factored to give a new matrix, the Factor Loading Matrix, of lower rank (less columns) which explains all the variation seen in the original data matrix. The rank or dimensions (no. of columns and rows) of the matrix is determined by the number of linearly independent vectors necessary to span the space containing the vectors of the matrix (Joreskog *et al.* 1976). The linearly independent vectors, the eigenvectors, U (the column vectors of the Factor Loading Matrix), and the associated eigenvalues, λ , are obtained by algebraically solving the equation

$$(H - \lambda I)U = 0$$

I=Identity matrix, the
analogue to the number 1
in scalar arithmetic

For example in a 2 x 2 matrix setting the determinant equal to zero and expanding gives

$$H - \lambda I = 0 \quad [\text{eqn. 1}]$$

$$\begin{vmatrix} h_{11} - \lambda & h_{12} \\ h_{21} & h_{22} - \lambda \end{vmatrix} = 0$$

$$(h_{11} - \lambda)(h_{22} - \lambda) - h_{12}h_{21} = 0$$

$$(\lambda^2 - \lambda(h_{11} + h_{22}) + (h_{11}h_{22} - h_{12}h_{21})) = 0$$

Solving the roots of the quadratic equation gives the two eigenvalues and substitution of the eigenvalues into [eqn. 1] gives rise to the eigenvectors. In Q-mode Factor Analysis the percentage of information explained in each eigenvector is simply:

$$\frac{\text{eigenvalue}}{\text{no. of rows in the Factor Loading matrix}}$$

The communality refers to the proportion of variation within a sample or row explained by the extracted factors. A communality of 1 indicates that all the variation is explained by the extracted factors. The departure from unity is a measure to which the sample deviates from the plane on which its projected. The Factor Scores Matrix associated with the Factor Loading Matrix are the positions of the variables on Factor 1, the first eigenvector, etc.

Two factors from both the S. Uplands Ordovician-Midland Valley Factor Loading Matrix and the S. Uplands Silurian-Midland Valley Factor Loading Matrix were retained for rotation. Orthogonal simple rotation, varimax rotation, through a rigid frame changes the Factor Loading Matrix so the factors have a high positive or a high negative loading and many zero or close to zero loadings. This produces a vector loading on a given factor where the variance will be at a maximum. An extensive mathematical treatment of varimax rotation can

be found in Harman (1960).

The two factors retained for rotation account for at or close to 90% of the variation in both the Ordovician-Midland Valley and Silurian-Midland Valley sediments and suggest that each set of data can be equated with two distinct end members. Communalities of all the samples on the first two factors is close to 1, so the samples define vectors that plot as radii of a circle, Figs. (4.4.1-4.4.2). The associated Factor Scores Matrices are given in Tables (4.4.1-4.4.2).

In both cases, the Straiton samples can be regarded as one compositional end member and the Ordovician and Silurian samples the second compositional end member, respectively. The Factor Scores Matrix for the Ordovician-Midland Valley sediments shows the position of the samples along Factor 1 are determined mainly by metamorphic rock fragments and to a lesser extent by total quartz. The position of the samples along Factor 2 is controlled mainly by the amount of matrix and lower but equal amounts of both acid volcanics and feldspar. Basic igneous fragments are not represented where a third compositional end member rich in both acid and basic fragments is suggested by samples occurring in the negative field of Factor 1 and a larger departure from unity in the Ordovician samples. In the Silurian-Midland Valley sediments Factor 1 is associated with metamorphic rock fragments and total quartz as well as feldspar. Factor 2 is associated with matrix and equally by the presence of acid volcanics and basic volcanics.

The Southern Uplands sediments are therefore considerably richer in matrix and volcanics than the Midland Valley clasts. In both cases, the Midland Valley clasts show a closer similarity to the compositional end member effectively defined by the Straiton samples. The separation is particularly strong in the Silurian-Midland Valley comparison, (Fig. 4.4.2) where almost all the variation is accounted for in the two Factors. Compared to the Silurian sediments all but a few samples from the Midland Valley cluster into a group which has higher amounts of metamorphic fragments, total quartz and feldspar. The Ordovician sediments in contrast have higher amounts of feldspar and acid volcanics than the Midland Valley clasts. The Ordovician samples plot at high Factor 2 values and it is interesting that Midland Valley clasts plot close to the Factor 2 compositional end member for the Ordovician sediments (Fig. 4.4.1) but do not plot close to the Silurian Factor 2 compositional end member in Fig. (4.4.2). This may suggest that a few of the Midland Valley clasts have a stronger similarity to the Ordovician sediments, particularly the quartz-rich Ordovician sediments, than to the Silurian sediments.

A scattergram plot of the mean value of Factor 2 taken from the Ordovician-Midland Valley Factor Loading Matrix for each area in the Midland Valley is given in Fig. (4.4.3).

The similarity to the Ordovician sediments, which is in effect a decrease in the compositional and textural maturity of the samples, increases from the Straiton to the Tinto-Carmichael samples. The North Esk samples have a slightly lower mean Factor 2 value and indicate a change again towards increasing maturity and away from the Ordovician sediments. This trend is again seen in the geochemistry of the sediments, chapter 5.

4.5. Conclusions.

1). Sandstone clasts within the Greywacke Conglomerate are immature arenites and wackes initially deposited as flysch sediments.

2). Samples from the Straiton area are almost solely derived from a metamorphic source. Samples from section 1 are exceptionally rich in metaquartz-arenites and devoid of volcanics whereas samples from section 2 are rich in low-grade schists and feldspathic-quartzites and have a very slight enrichment in volcanic fragments.

3). There is a systematic increase in volcanic and associated decrease in metamorphic fragments from the Hagshaw Hills through to the North Esk samples. However, all the samples show a significant contribution from a metamorphic terrane.

4). The majority of volcanic fragments in all the areas are acidic, particularly in the North Esk where mature acid volcanics, *e.g.* rhyolites, are common. The highest percentage of basic fragments are found in both the Tinto-Carmichael and North Esk regions. The Tinto-Carmichael samples are finer grained than the North Esk samples and coarse-grained samples would be expected to be richer in basic fragments than equivalent coarse-grained samples from the North Esk area.

5). Only the most siliceous sediments from the S. Uplands Ordovician have a comparable mineralogy to the Midland Valley greywacke clasts.

6). A strong similarity in compositional maturity exists between the S. Uplands Silurian Central Belt sediments and the Midland Valley greywacke clasts. However there are significant differences in the overall mineralogy.

7). The Midland Valley greywacke clasts are more closely related to each other than to either the S. Uplands Silurian or Ordovician sediments. However, clasts with the highest percentage of basic fragments from the Midland Valley more closely resemble the siliceous Ordovician sediments in overall mineralogy, *e.g.* low sedimentary and higher metamorphic fragments, than the Silurian sediments.

Sources for figures in Chapter 4

Fig. 4.3.7 Modified from Leggett *et al.* (1979)

Fig. 4.3.8 Ordovician data from Floyd (1975), Welsh (1964), Kelling (1958)

Fig. 4.3.9 Ordovician data from Floyd (1975) and Kelling (1958)

Fig 4.3.10 Silurian data from Casey (1984), Warren (1963), Gordon (1962) and Walton (1955)

Fig. 4.3.11 Silurian data from Casey (1984) and Gordon (1962)

Fig. 4.3.12 Silurian data from Gordon (1962)

Fig 4.4.1 Ordovician data from Floyd (1975), Welsh (1964), and Kelling (1958)

Fig 4.4.2 Silurian data from Warren (1963), Gordon (1962) and Walton (1955)

Fig. 4.1.1 X-ray diffractograms from sample 16h1 and representative of the Greywacke Conglomerate as a whole.

(a.-d.) 1-0.5 μ

a).: untreated except removal of carbonate by triammonium citrate

b).: glycolated;

c).: heated at 250° c for 1 hr.;

d).: heated at 525° c for 1 hr

e). 1.0-2.0 μ

untreated except removal of carbonate by triammonium citrate

f). 2.0-5.0 μ

untreated except removal of carbonate by triammonium citrate

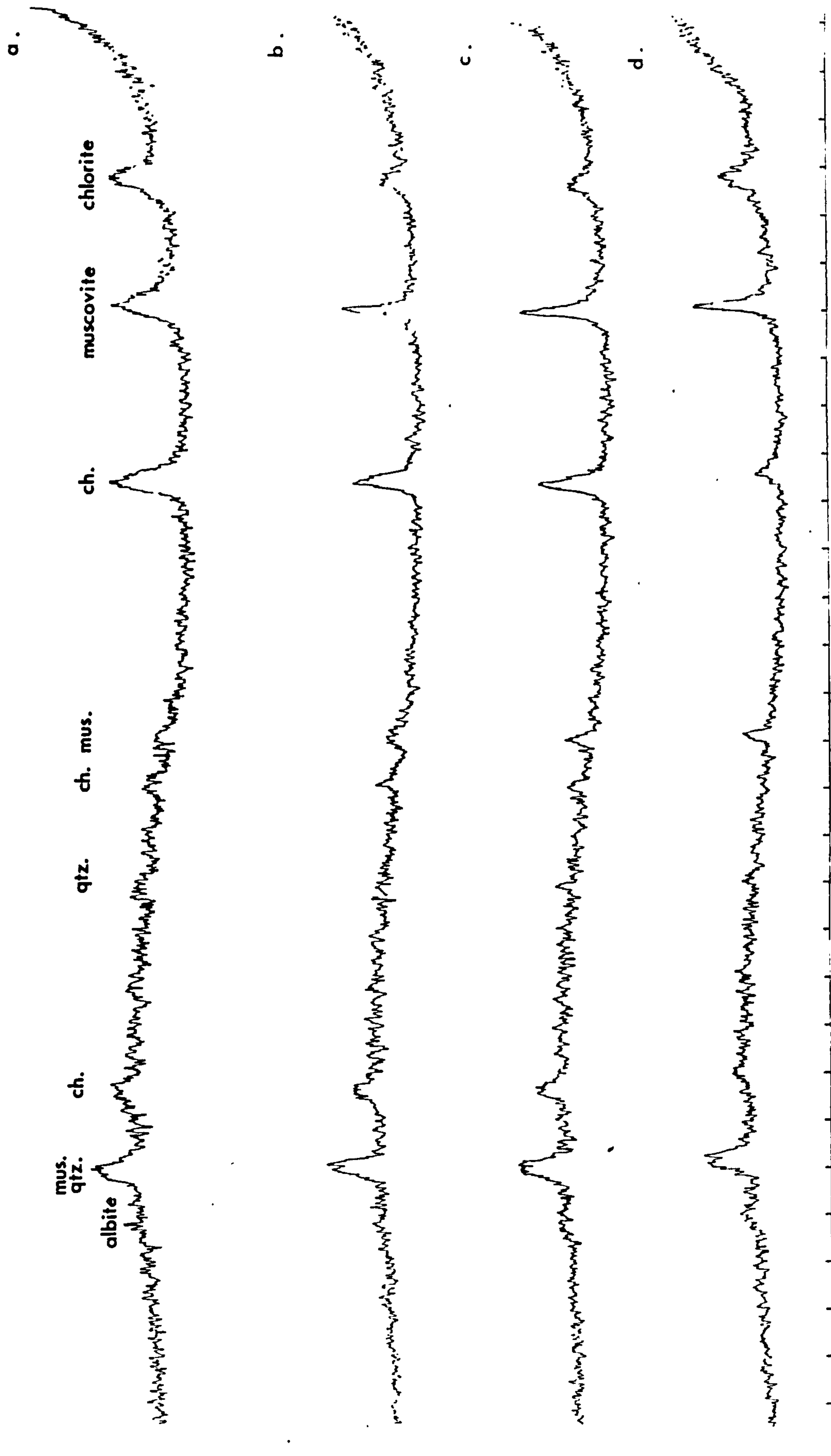


Fig. 4.1.1

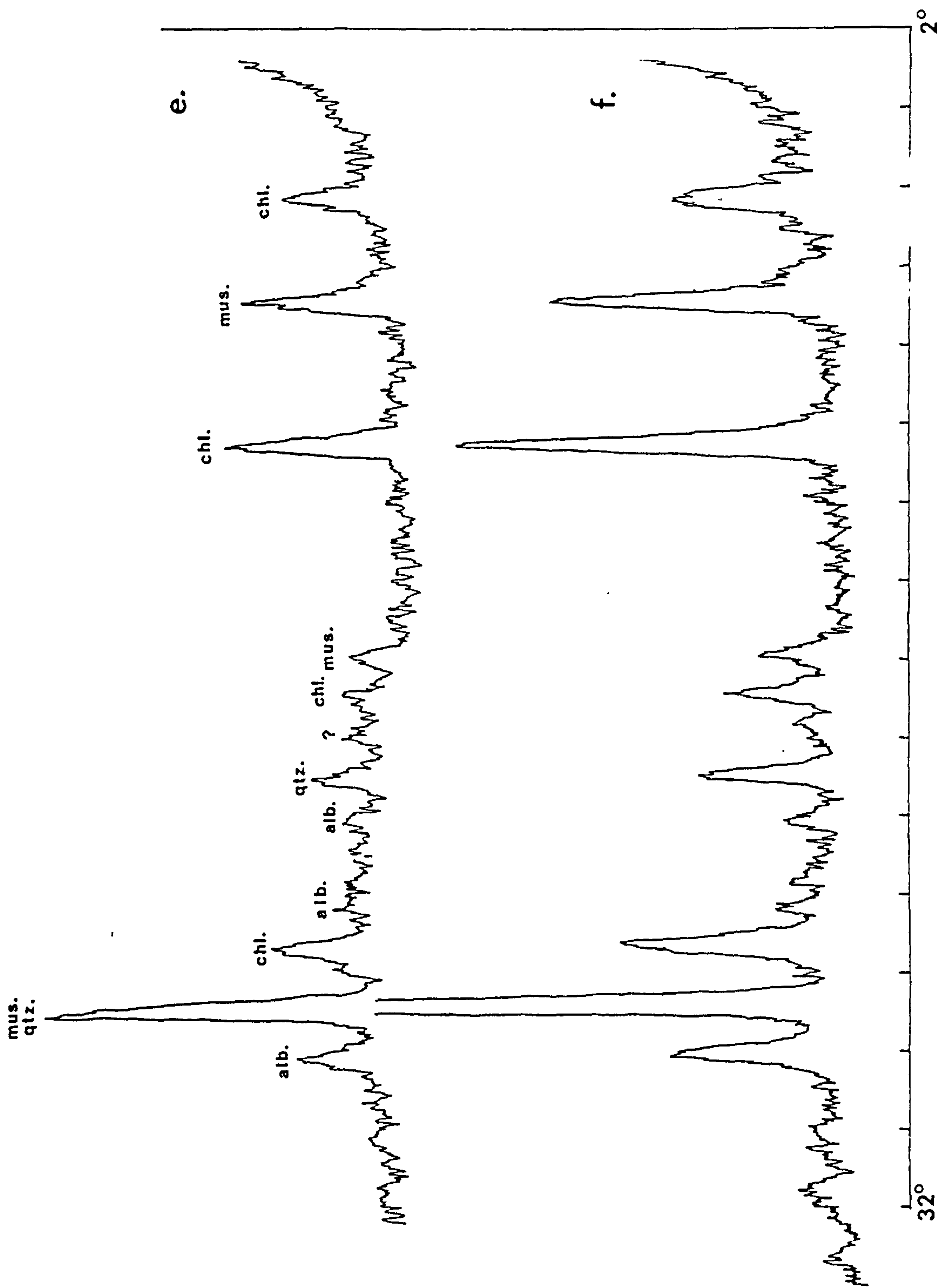


Fig. 4.1.1 cont.

Table 4.3.1

Petrographic analysis: Mean values of major groups and subgroups

| | Str | HH | T | C | NE |
|-----------------|--------|--------|--------|--------|--------|
| Quartz | | | | | |
| Total | 43.99% | 40.17% | 36.77% | 40.75% | 38.87% |
| Mono | 73.24% | 77.81% | 75.92% | 77.36% | 77.70% |
| Poly | 26.59% | 21.12% | 23.91% | 22.34% | 22.10% |
| Chert | 0.17% | 1.07% | 0.17% | 0.30% | 0.20% |
| Feldspar | | | | | |
| Total | 10.41% | 13.95% | 17.08% | 18.66% | 18.93% |
| Twinned | 7.62% | 13.95% | 10.05% | 14.81% | 10.17% |
| Untwinned | 86.28% | 77.69% | 86.04% | 77.16% | 86.06% |
| Perthite | 3.04% | 4.50% | 3.45% | 6.85% | 1.97% |
| Microcline | 0.40% | 0.55% | 0.30% | 1.18% | 0.53% |
| Ca-Altered | 2.66% | 3.32% | 0.15% | 0.00% | 1.27% |
| Volcanic Basic | | | | | |
| Total | 0.28% | 1.23% | 3.45% | 2.21% | 2.60% |
| Volcanic Acidic | | | | | |
| Total | 1.48% | 4.94% | 3.93% | 4.09% | 3.59% |
| Felsitic | 68.22% | 47.71% | 84.55% | 43.47% | 69.01% |
| Crs Felsitic | 15.44% | 18.34% | 5.28% | 14.79% | 9.24% |
| Microlitic | 1.94% | 6.33% | 1.67% | 10.83% | 2.36% |
| Rhyolitic | 9.37% | 13.47% | 6.11% | 24.36% | 14.66% |
| Qtz-Fld | 5.03% | 14.16% | 2.40% | 6.55% | 4.72% |
| Metamorphic | | | | | |
| Total | 18.63% | 11.10% | 13.11% | 10.69% | 11.19% |
| Phyllite/Grit | 3.89% | 5.85% | 3.36% | 0.00% | 4.92% |
| Schist/Gneiss | 42.94% | 20.19% | 36.21% | 26.26% | 38.57% |
| Quartzite | 53.17% | 73.96% | 60.43% | 73.74% | 56.51% |

Table 4.3.1 (cont.)

| | Str | HH | T | C | NE |
|--------------|--------|--------|--------|---------|--------|
| Sedimentary | | | | | |
| Total | 0.09% | 0.24% | 0.13% | 0.04% | 0.04% |
| Altered | | | | | |
| Total | 4.24% | 4.80% | 4.43% | 4.22% | 4.84% |
| Sericite-Alt | 51.89% | 59.99% | 83.52% | 81.12% | 69.88% |
| Ca-Alt | 31.61% | 13.88% | 4.67% | 0.00% | 6.57% |
| Chlorite-Alt | 12.45% | 19.88% | 9.41% | 15.05% | 17.28% |
| Oxide-Alt | 4.05% | 6.25% | 2.41% | 3.82% | 6.27% |
| Matrix | | | | | |
| Total | 11.19% | 8.92% | 16.61% | 13.87% | 13.51% |
| Cement | | | | | |
| Total | 6.72% | 10.70% | 1.79% | 2.19% | 3.66% |
| Ca-Cmt | 57.46% | 45.28% | 9.82% | 0.00% | 9.74% |
| Oxide-Cmt | 42.54% | 54.72% | 90.18% | 100.00% | 90.26% |
| Veins | | | | | |
| Total | 0.51% | 1.09% | 0.00% | 0.00% | 0.89% |
| Ca-Vein | 81.31% | 77.50% | 0.00% | 0.00% | 67.91% |
| Qtz-Vein | 18.69% | 22.50% | 0.00% | 0.00% | 32.09% |
| Accessories | | | | | |
| Total | 2.47% | 2.87% | 2.71% | 3.29% | 1.87% |
| Oxide-Acc | 18.42% | 24.30% | 10.15% | 19.40% | 11.77% |
| Mica-Acc | 68.45% | 67.78% | 46.58% | 31.54% | 54.95% |
| Epidote-Acc | 0.00% | 0.00% | 12.00% | 14.35% | 13.76% |
| Other-Acc | 13.14% | 7.92% | 31.28% | 34.71% | 19.52% |

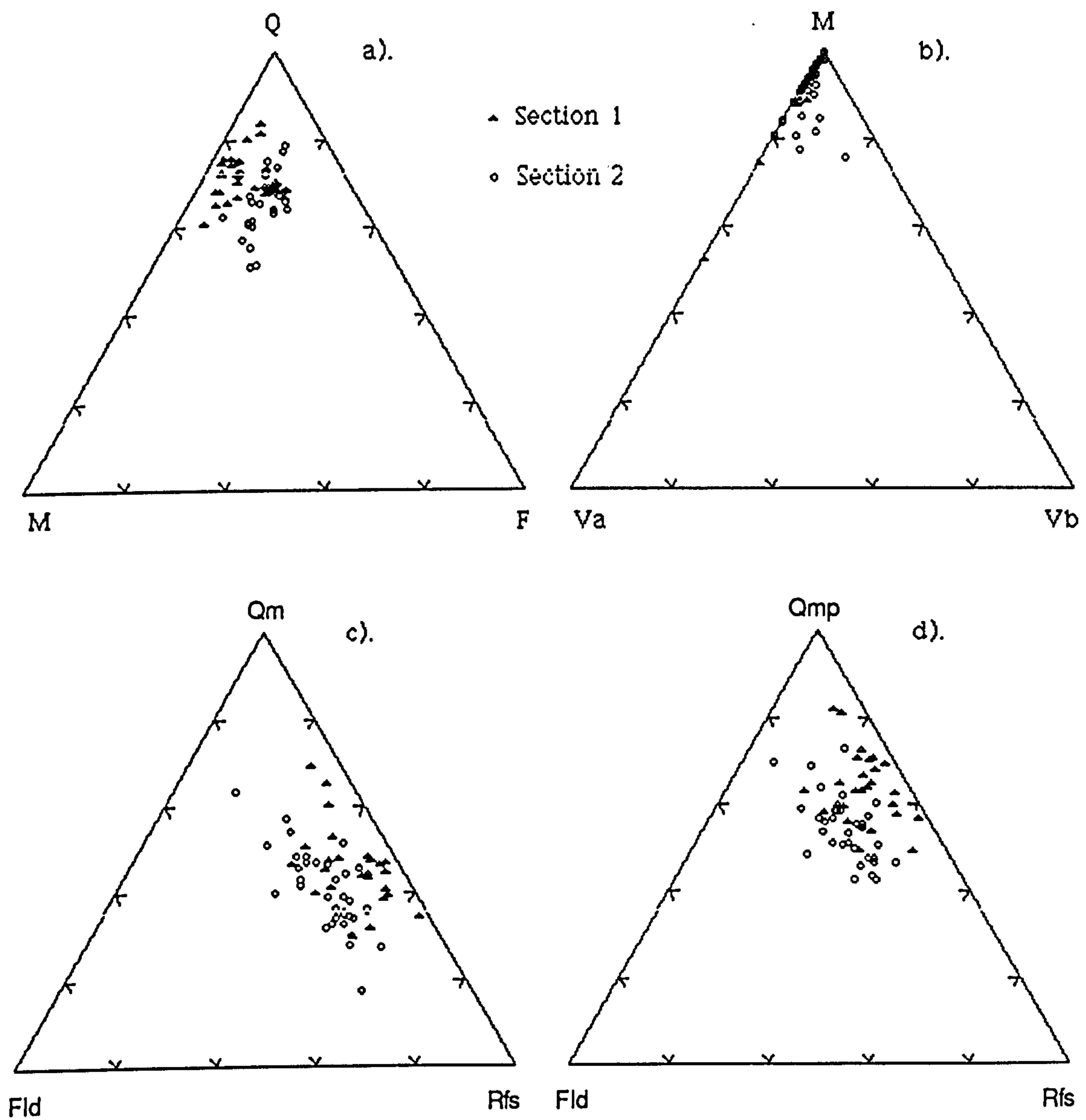


Fig. 4.3.1 Petrographic modal composition of Straiton samples

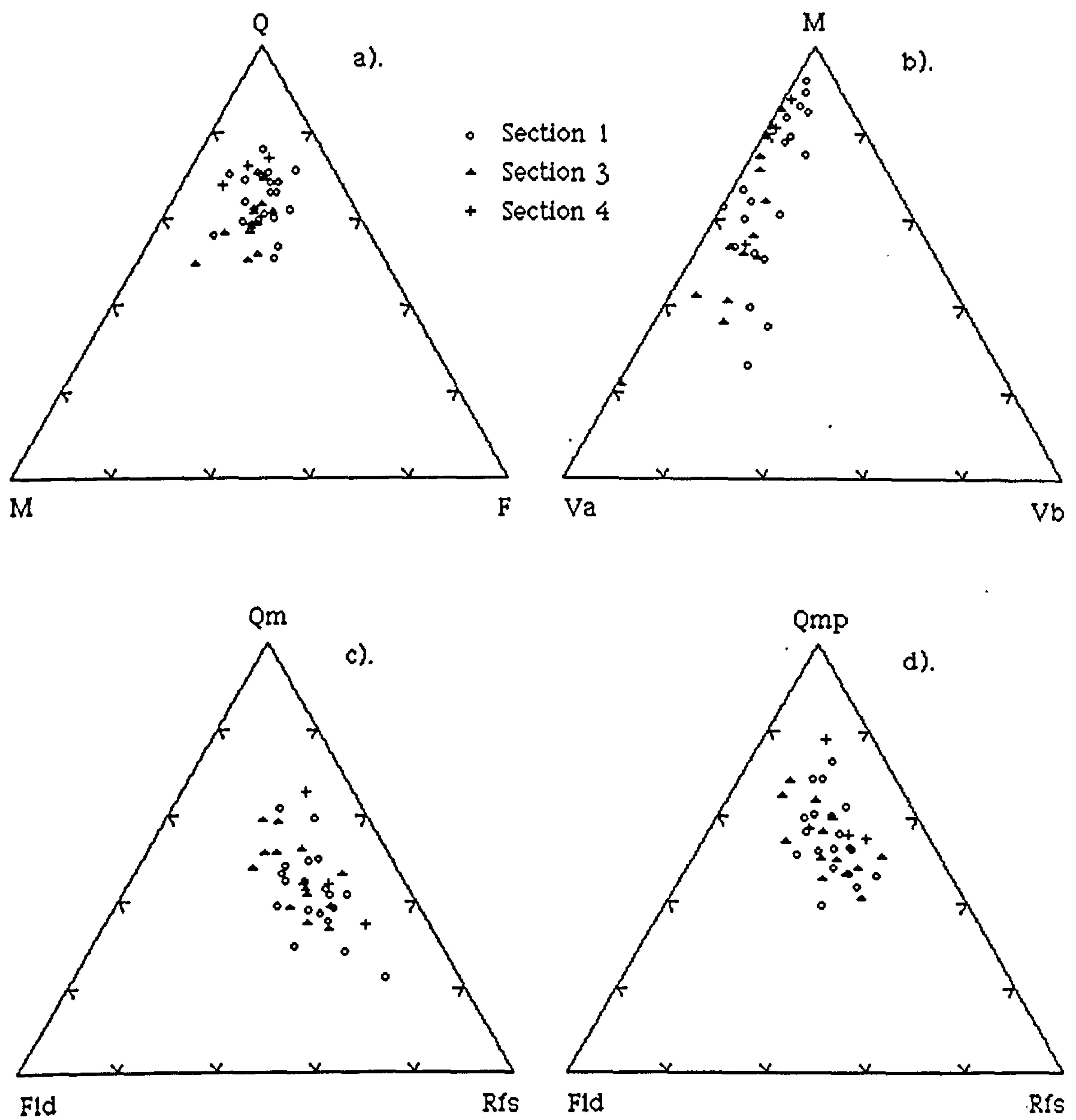


Fig. 4.3.2 Petrographic modal composition of Hagshaw Hills samples

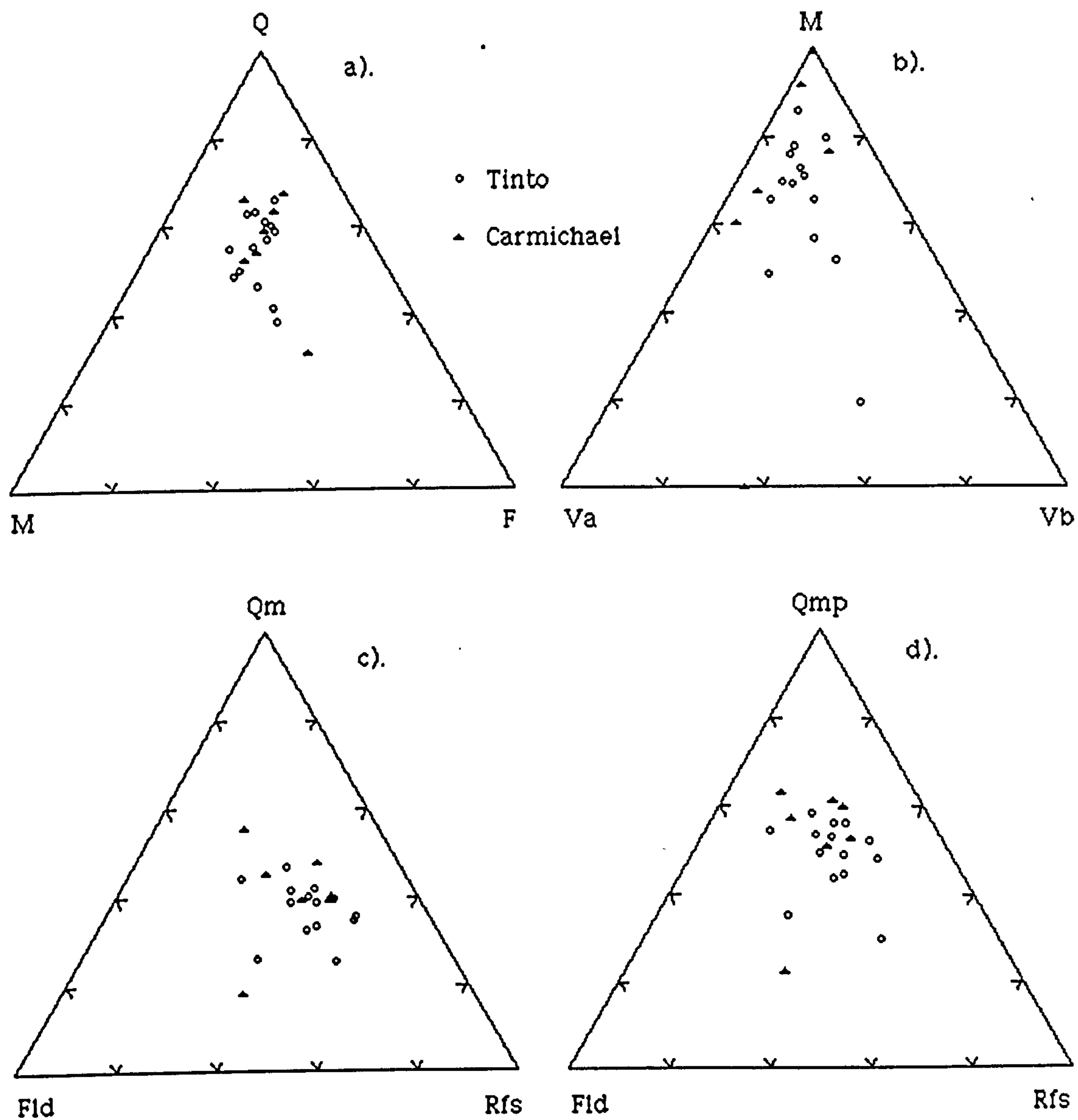


Fig. 4.3.3 Petrographic modal composition of Tinto and Carmichael samples

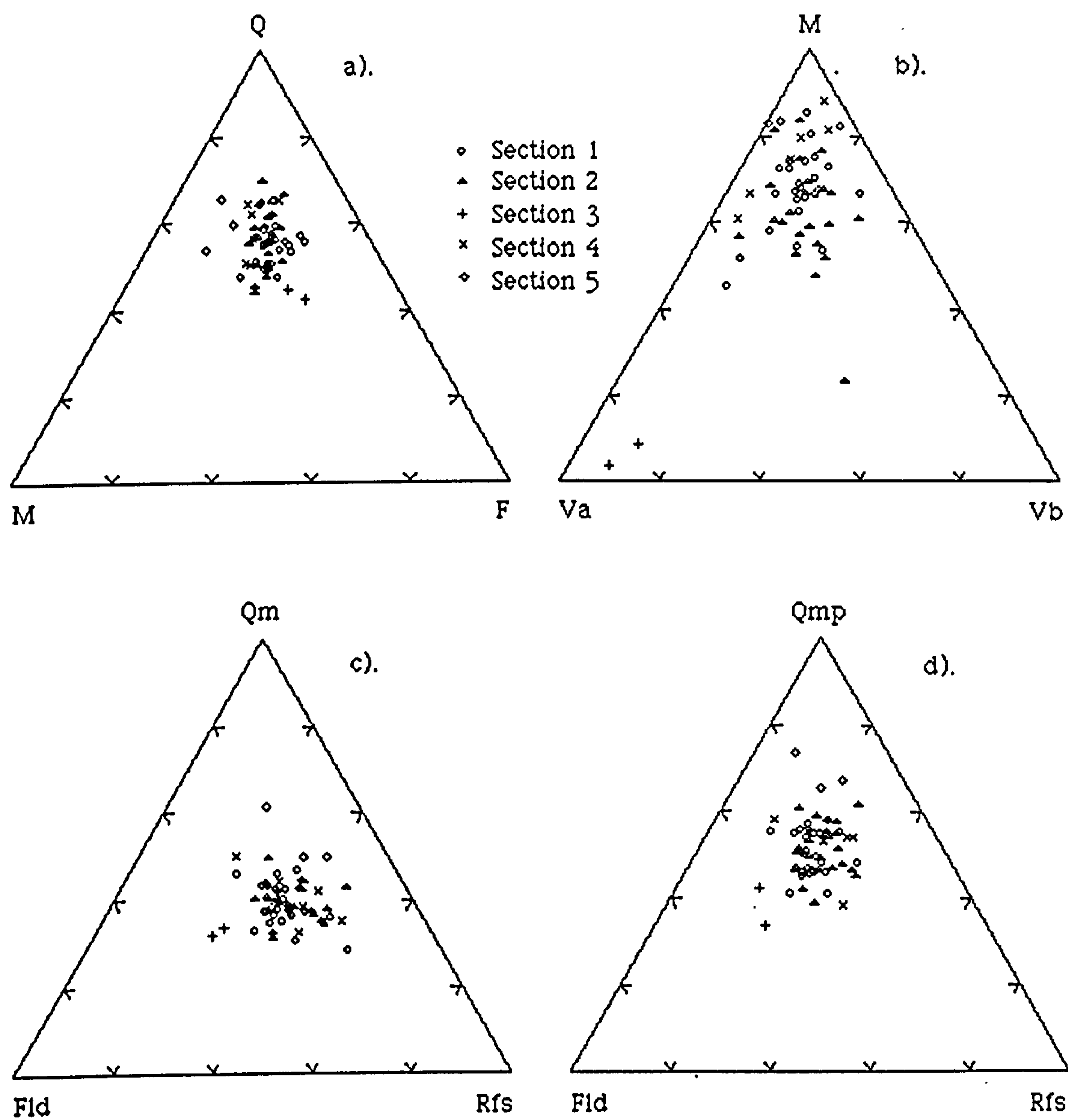
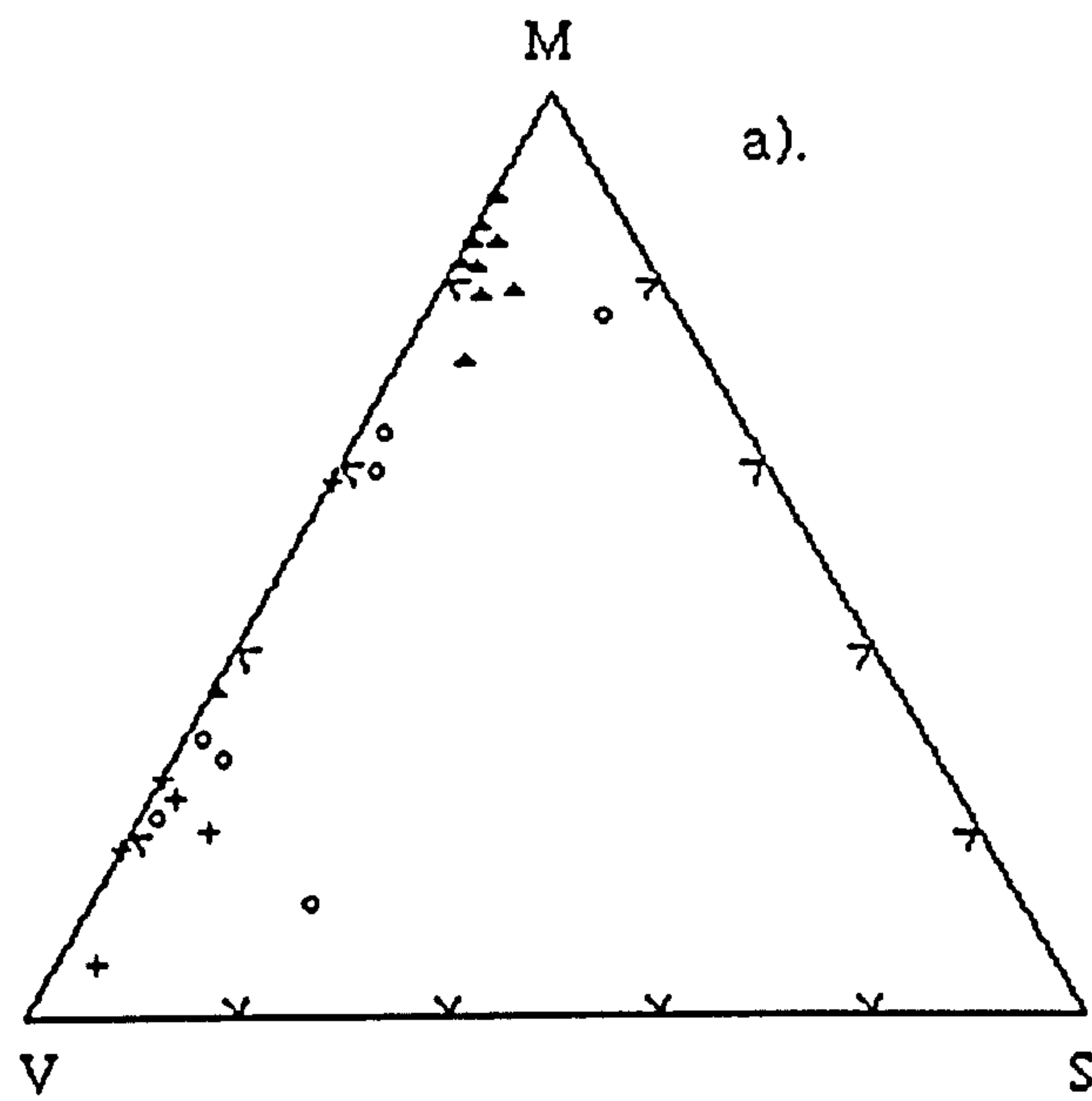


Fig. 4.3.4 Petrographic modal composition of North Esk samples



- ▲ Straiton
- Hagshaw Hills
- + North Esk

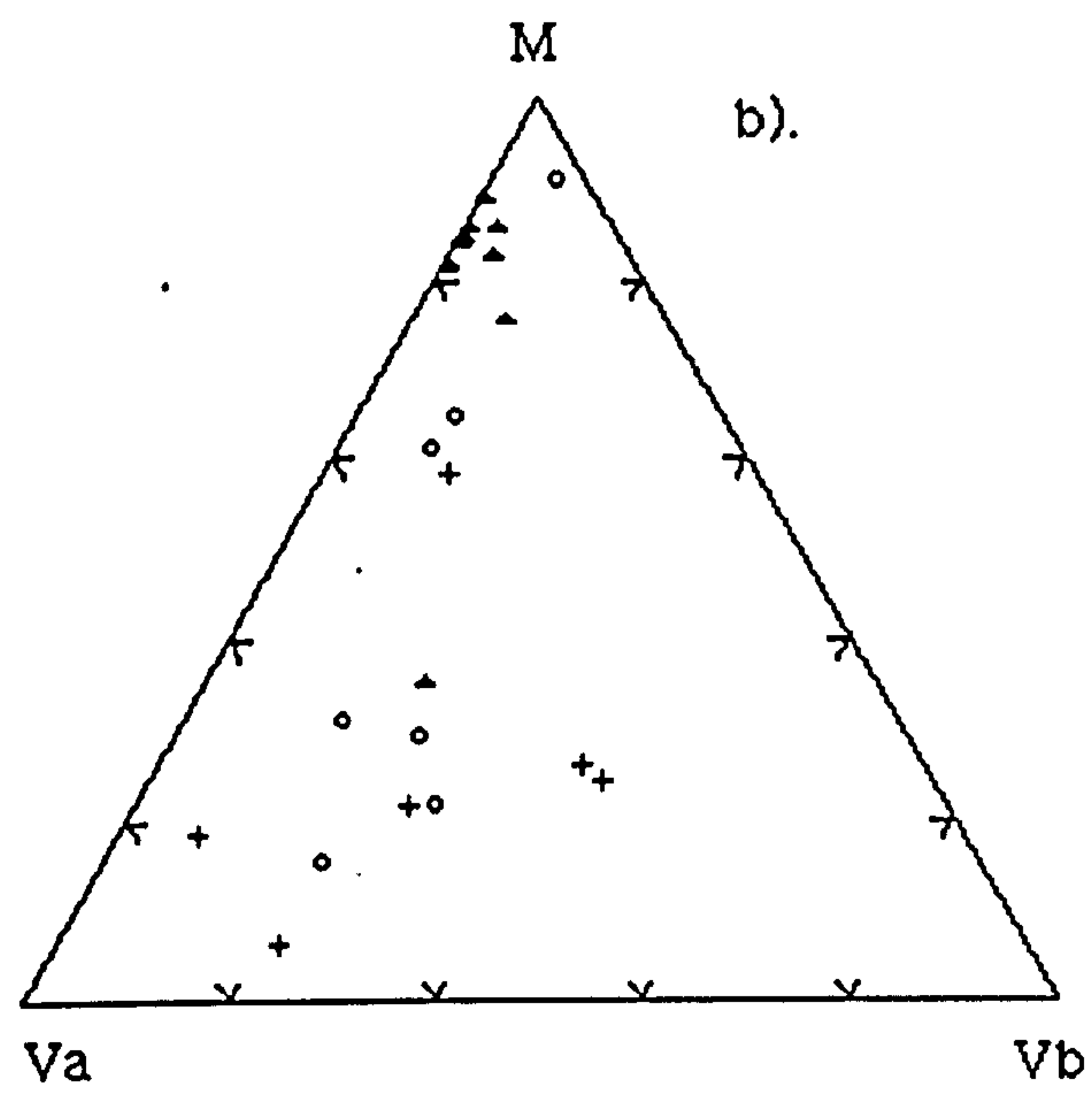


Fig. 4.3.5 Granule modal composition of Midland Valley greywacke clasts.

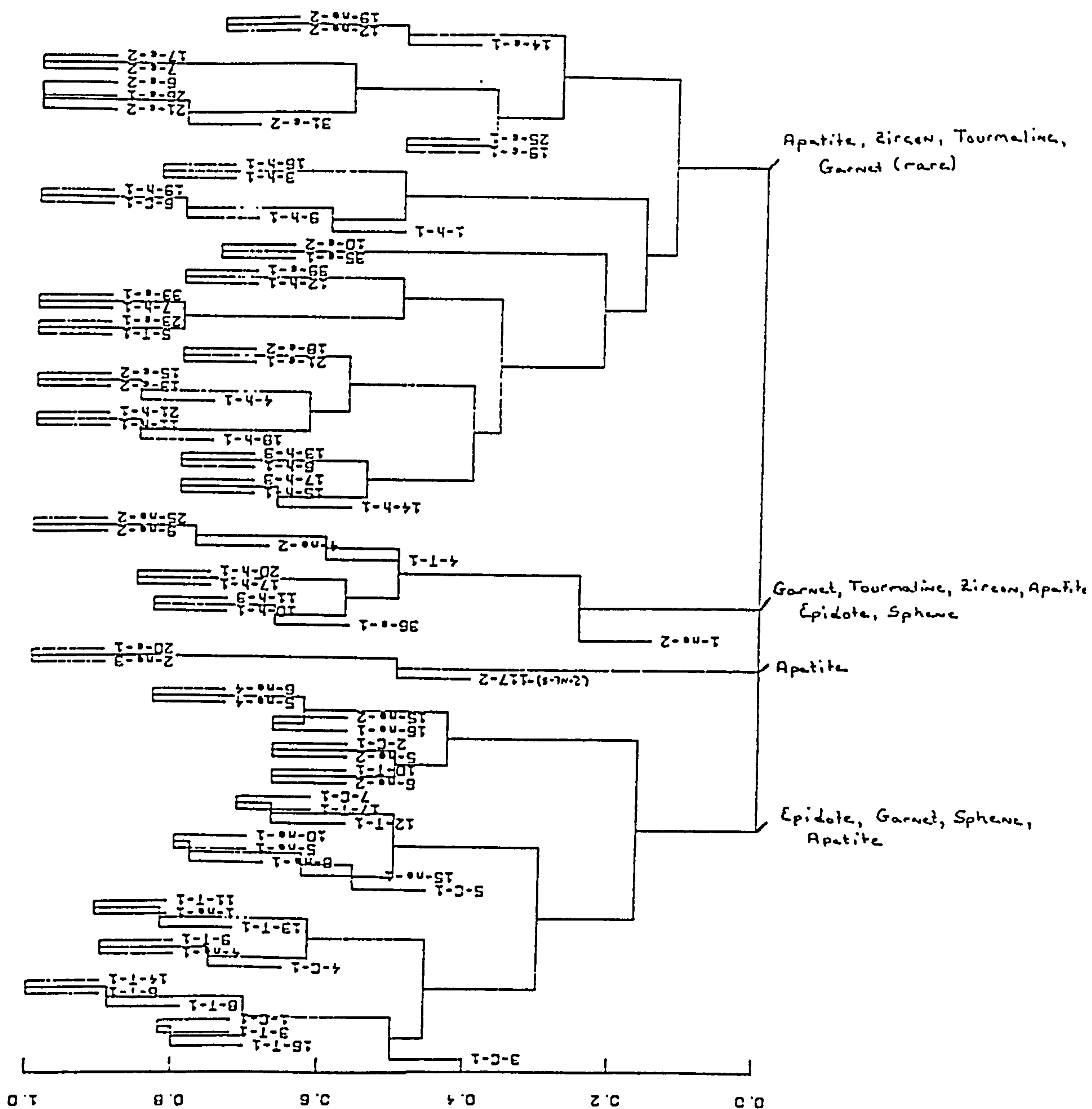


Fig. 4.3.6 Cluster dendrogram of heavy mineral suites in Greywacke Conglomerate sandstone clasts.

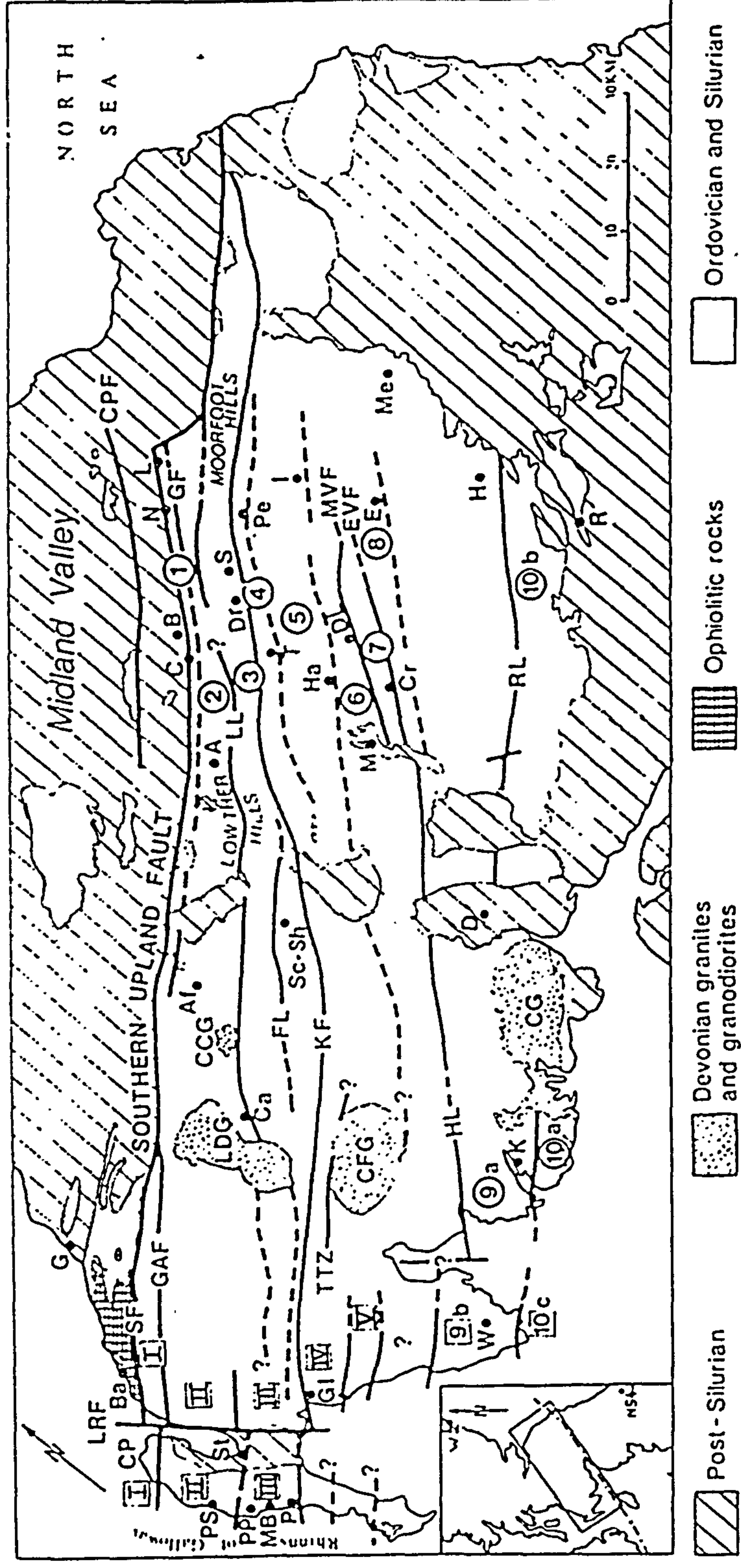


Fig. 4.3.7a. Geological map of the Southern Uplands, after Leggett, *et al.* 1980. Major reverse faults separate tracts with distinctive stratigraphic sequences (numbered as in 4.3.7). Solid lines show major faults (from published maps and papers; see Leggett, *et al.* 1980); dashed lines show inferred continuations from outcrops of basalt, chert and graptolitic shale (which occur in imbricate zones along the major faults), plotted from Geological Survey maps.

Faults: CPF-Carmichael-Pentland Fault; EVF Eltrick Valley Fault; FL Fardingmullach Line; GAF Glen App Fault; GF Grassfield Fault; RL Riccarton Line; SF Stinchar Fault; TTZ Talnotry Thrust Zone. **Place Names:** A Abington; Af Glen Aston dam; B Biggar; Ba Ballantrae; C Coulter; Ca Carsphairn; CP Corsewall Point; Cr Craigmichan; D Dumfries; DL Dobbs Linn; Dr Drummelzier; E Ettrickbridgend; G Girvan; GI Glenluce; H Hawick; Ha Harfell; I Innerleithen; K Kirkcudbright; L Leadburn; M Moffat; MB Morroch Bay; Me Melrose; N Noblehouse; P Portayew; Pe Peebles; PP Portpatrick; PS Portlògan; R Riccarton; S Stobo; Sc-Sh Scar-Shinnel; St Stranraer; T Talla/Tweedsmuir; W Whithorn. **Devonian Granites:** CCG Cairnsmore of Carsphairn; CFG Cairnsmore of Fleet; CG Criffel; LDG Loch Doon.

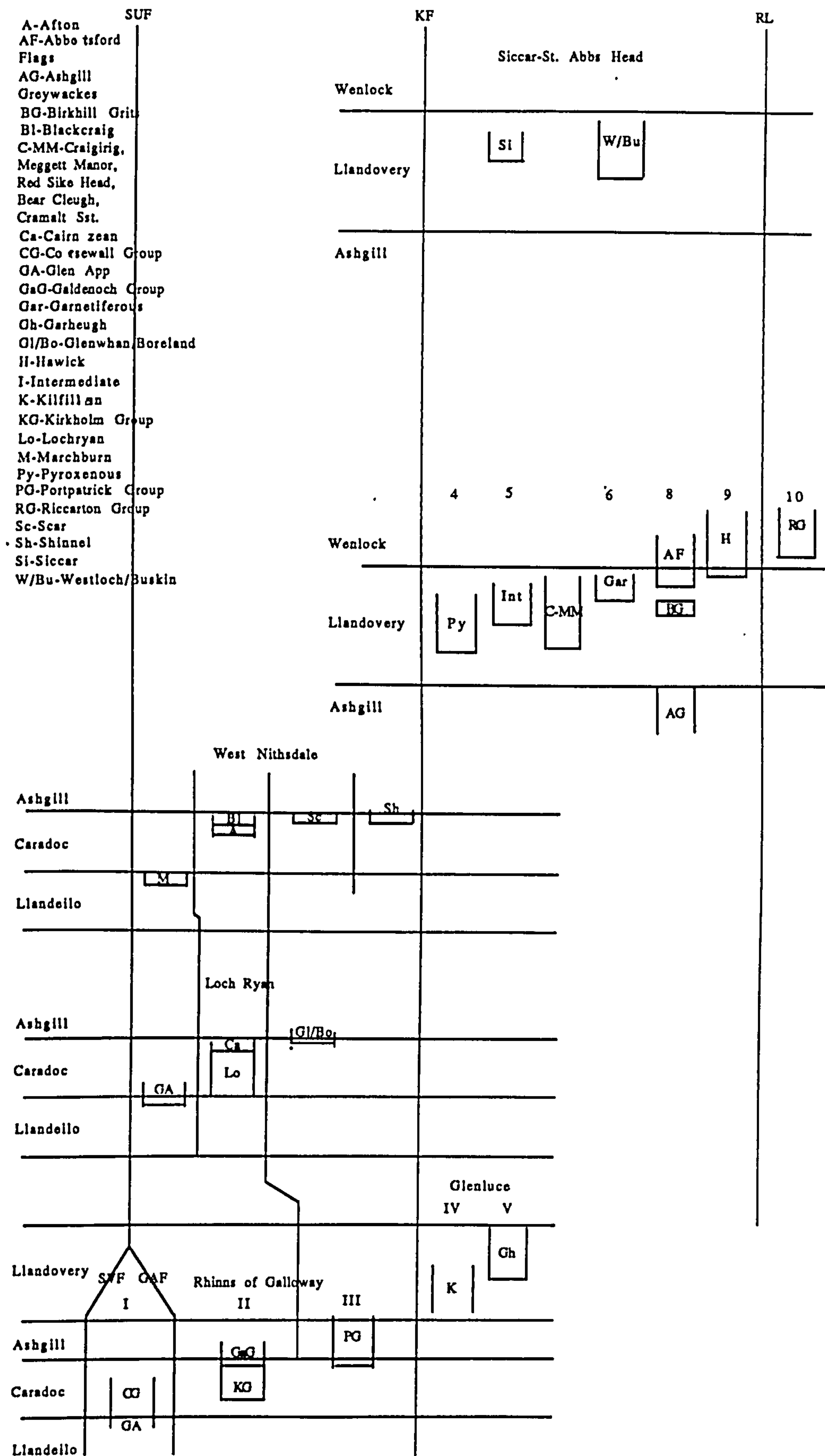


Fig. 4.3.7 Vertical sections through S. Uplands showing locations of coarse clastics used in this study

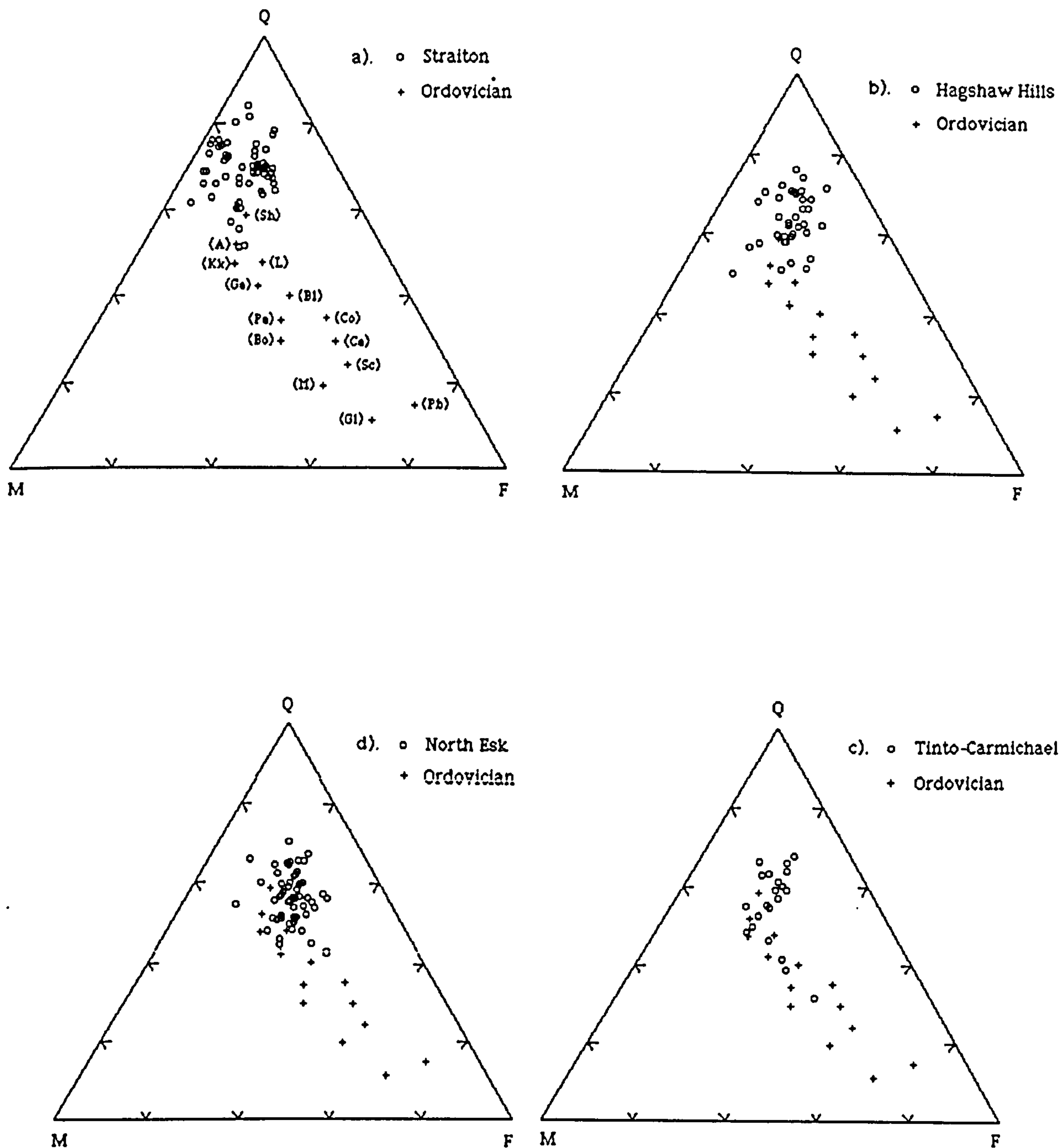


Fig. 4.3.8 Comparison of Southern Uplands Ordovician mean modal compositions and Midland Valley greywacke clasts

(A)- Afton Fm.
(Bl)-Blackraig Fm.
(Bo)-Boreland "Rocks"
(Ca)-Cairn Logan Group
(Co)-Corsewall Group
(Ga)-Galdenoch Group
(Gl)-Glenwhan "Rocks"
(L)-Lochryan "Rocks"
(M)-Marchburn Fm.
(Pa)-Portpatrick acid-clast Division
(Pb)-Portpatrick basic-clast Division
(Sc)-Scar Fm.
(Sh)-Shinnel Fm.

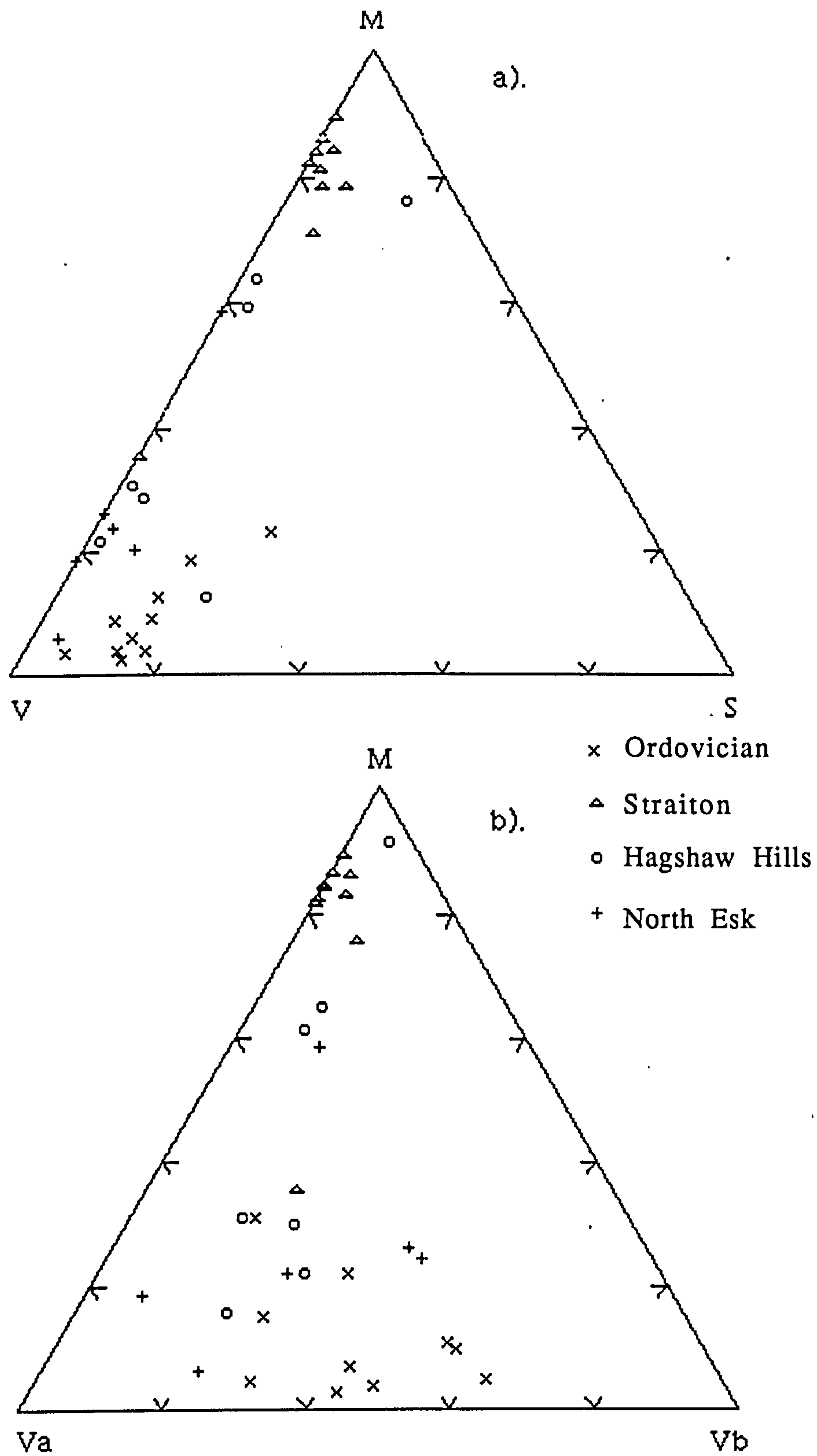


Fig. 4.3.9 Comparison of Southern Uplands Ordovician granule composition and Midland Valley greywacke clast granule composition

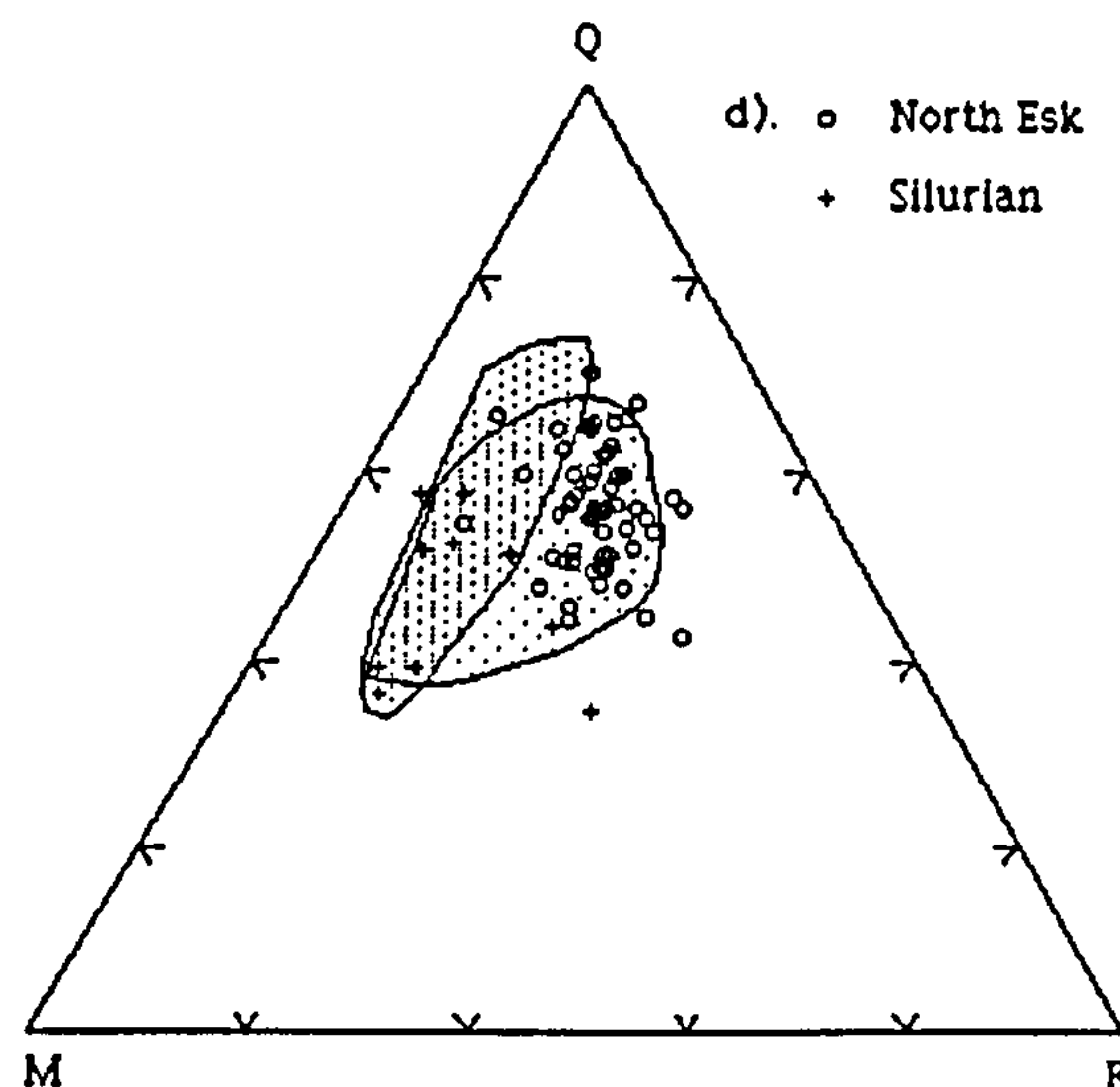
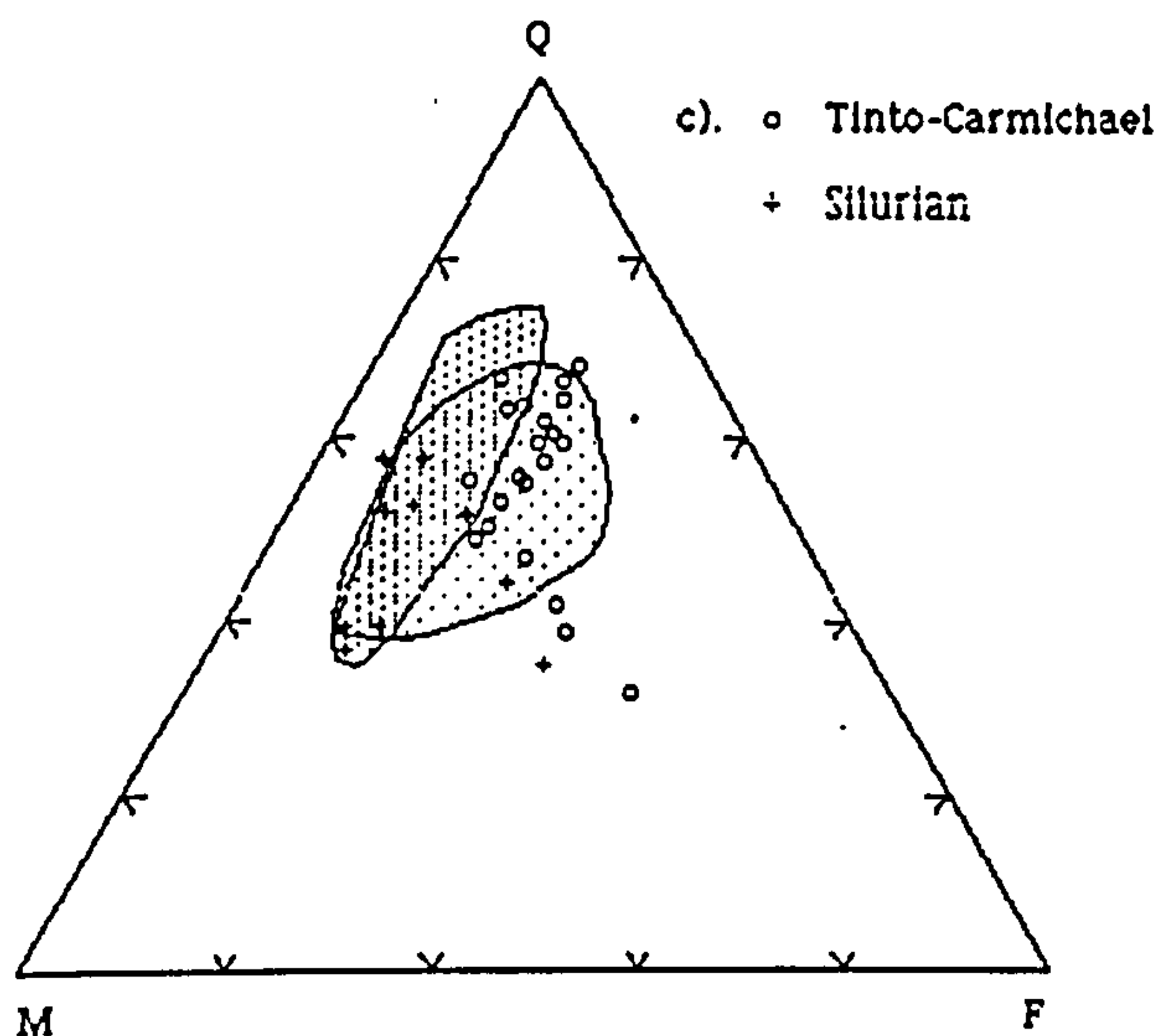
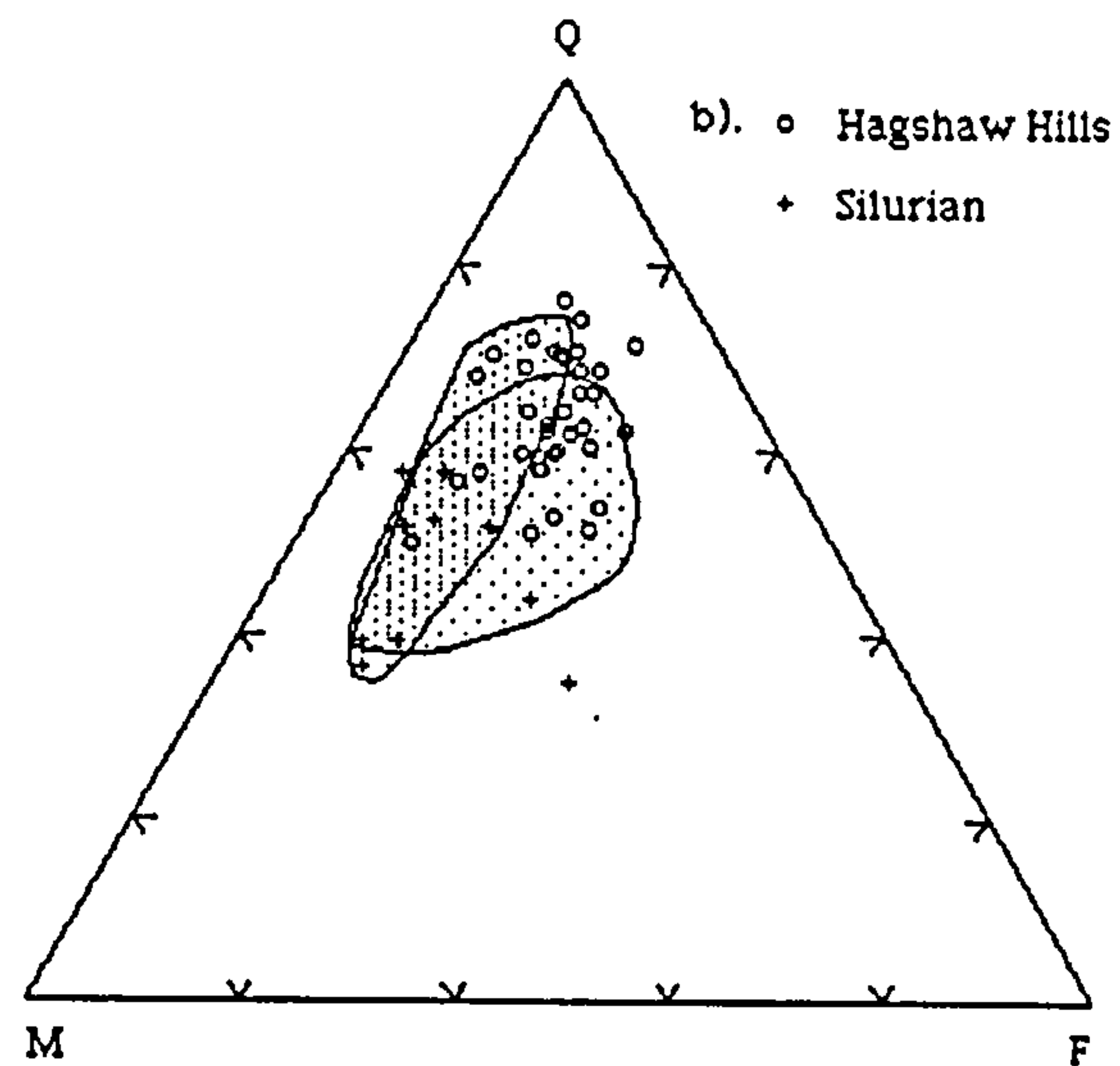
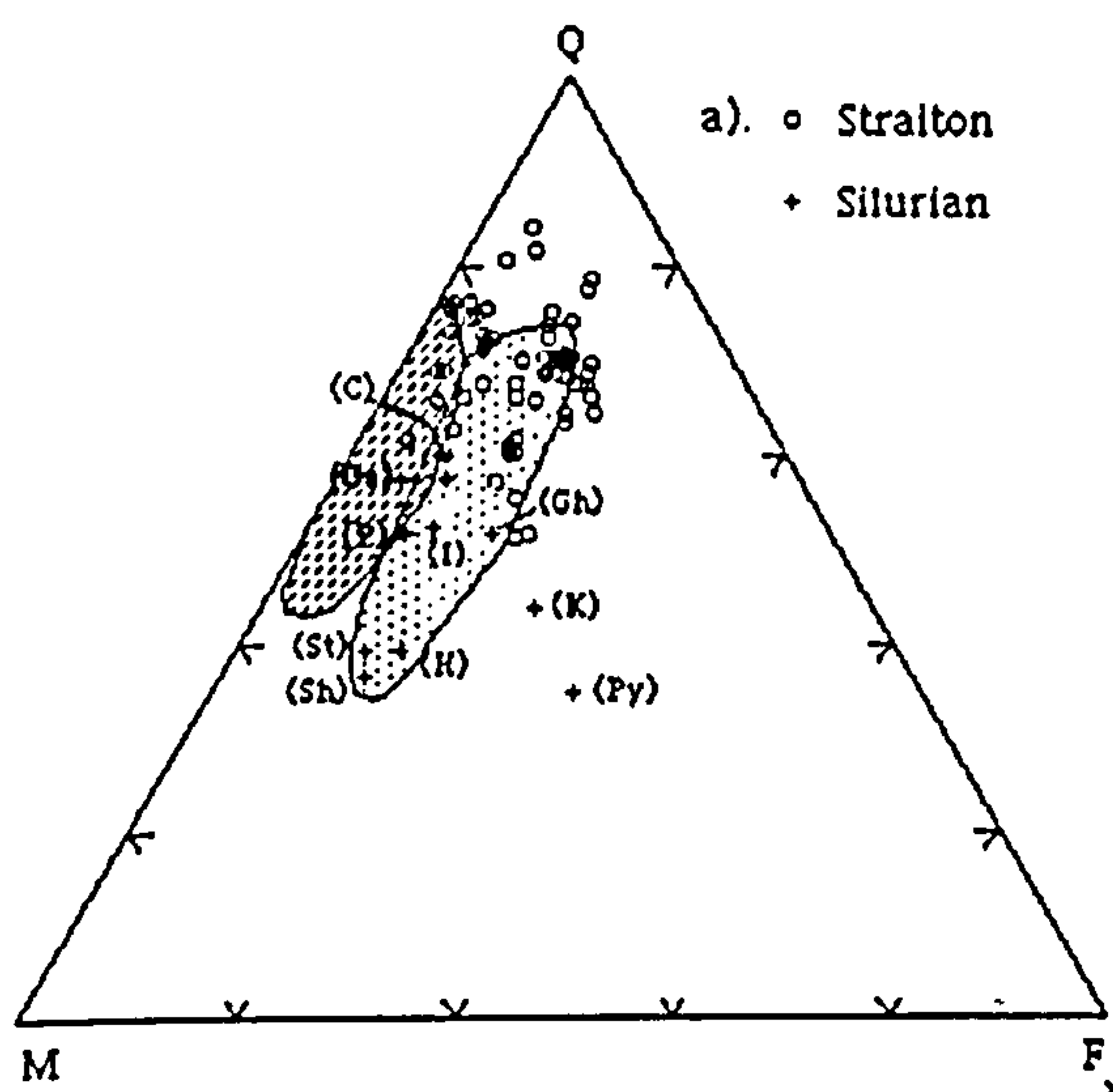
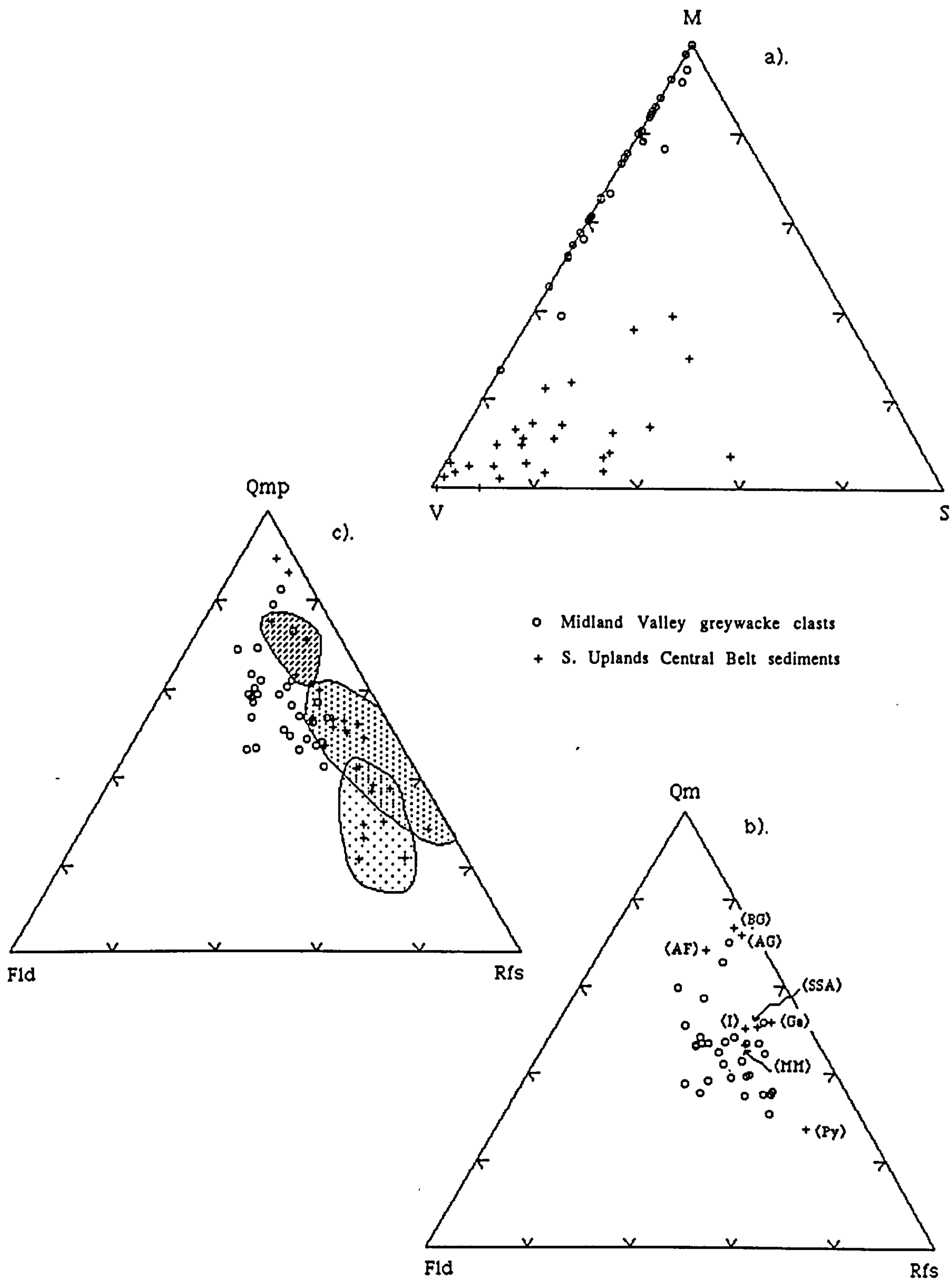


Fig. 4.3.10 Comparison of Southern Uplands Silurian mean modal compositions and Midland Valley greywacke clasts

▨ Field of Garnetiferous Gp ▤ Field of Intermediate Gp □ Field of Garheugh Fm.

(C)-Cauldron Burn Beds
(Ga)-Garnetiferous 'Group'
(Gh)-Garheugh Fm.
(H)-Hawick Rocks
(I)-Intermediate 'Group'
(K)-Killfillaun Fm.

(P)-Penchrise Burn Beds (Riccanton Group)
(Py)-Pyroxenous 'Group'
(Sh)-Shankend Beds (Riccanton Group)
(St)-Stobs Castle Beds (Riccanton Group)



▨ Field of Garnet. and Gala ▤ Field of Inter. and Garheugh ▤ Field of Pyrox. and Killfillian

Fig. 4.3.11

a-c). Comparison of 30 randomly selected Midland Valley greywacke clasts with i). 20 randomly selected samples from the Glenluce Killfillian and Garheugh Fms. and ii). mean modal compositions from the Pyr., Int., and Gar. Group greywackes, Gala Group greywackes (Meggett-Manor sst; Siccar-St Abbs) and tract 8 sediments (Birkhill Grits, Abbottsford Flags and Ashgill age greywackes)

b). Comparison of 30 randomly selected Midland Valley greywacke clasts with ii). as above

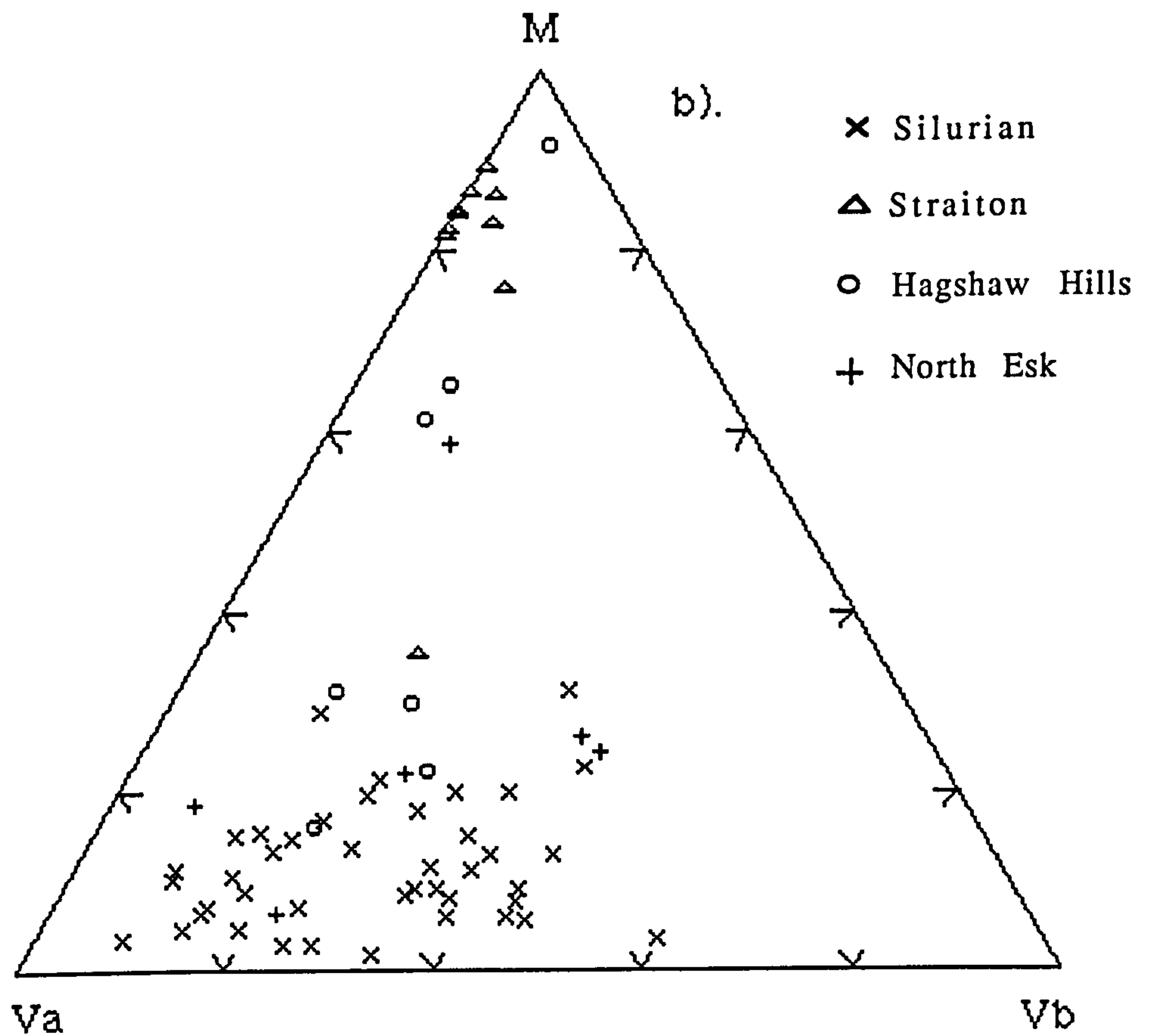
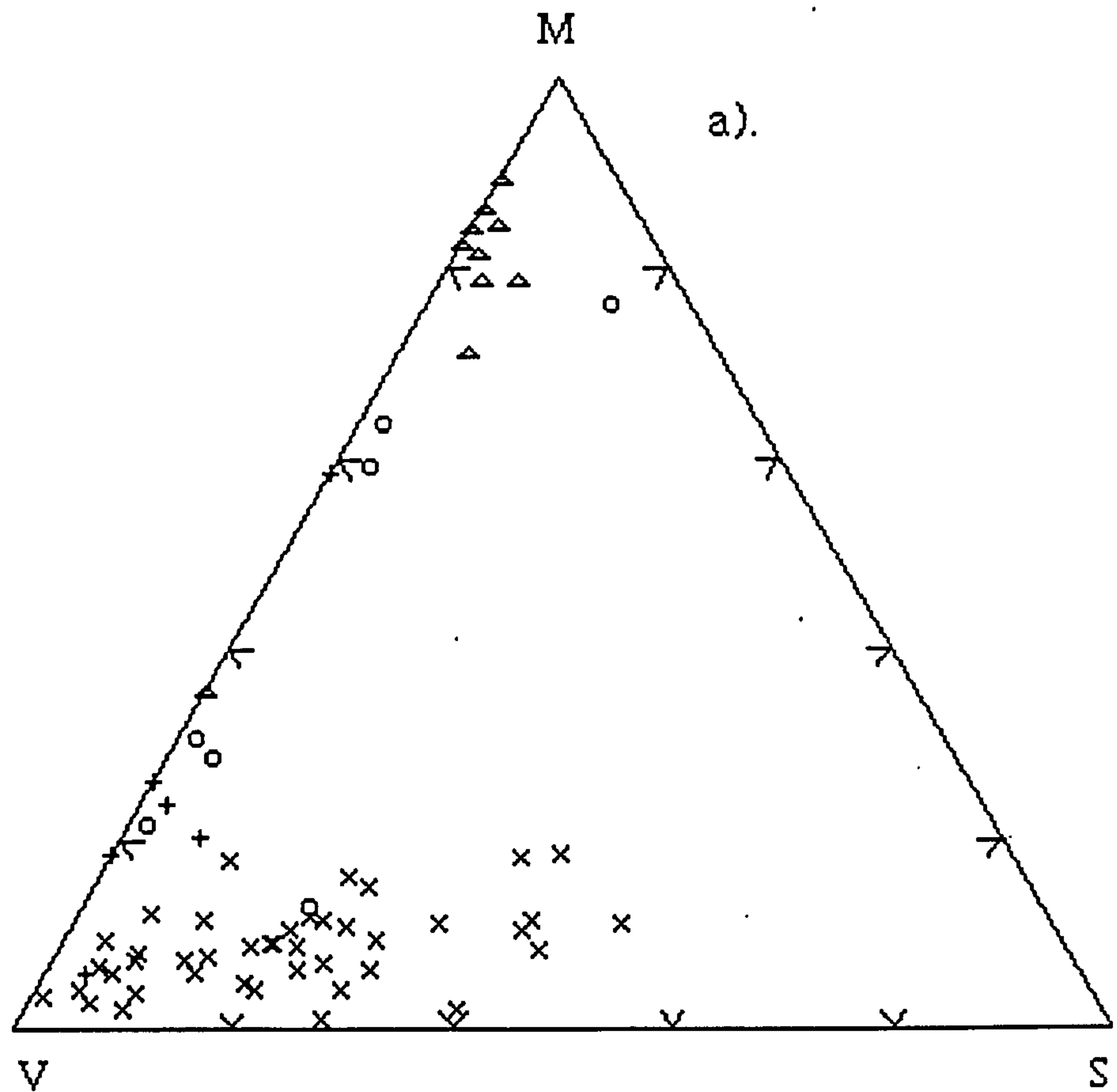


Fig. 4.3.12 Comparison of Southern Uplands Silurian granule composition and Midland Valley greywacke clast granule composition

Table 4.4.1

Ordovician-Midland Valley Rotated Factor Score Matrix

| | Factor 1 | Factor 2 |
|----------------|----------|----------|
| Q _T | 0.575 | 0.346 |
| Fld | -0.052 | 0.455 |
| V _b | -0.155 | 0.177 |
| V _a | -0.202 | 0.421 |
| Meta | 0.754 | 0.033 |
| Sed | -0.157 | 0.170 |
| Matrix | -0.093 | 0.660 |
| percent | 84.48% | 6.77% |

Table 4.4.2

Silurian-Midland Valley Rotated Factor Score Matrix

| | Factor 1 | Factor 2 |
|----------------|----------|----------|
| QT | 0.625 | -0.073 |
| Fld | 0.377 | -0.231 |
| V _b | -0.125 | -0.467 |
| V _a | -0.060 | -0.418 |
| Meta | 0.658 | 0.155 |
| Sed | -0.074 | -0.213 |
| Matrix | 0.100 | -0.692 |
| percent | 76.34% | 13.44% |

Midland Valley-SU Silurian

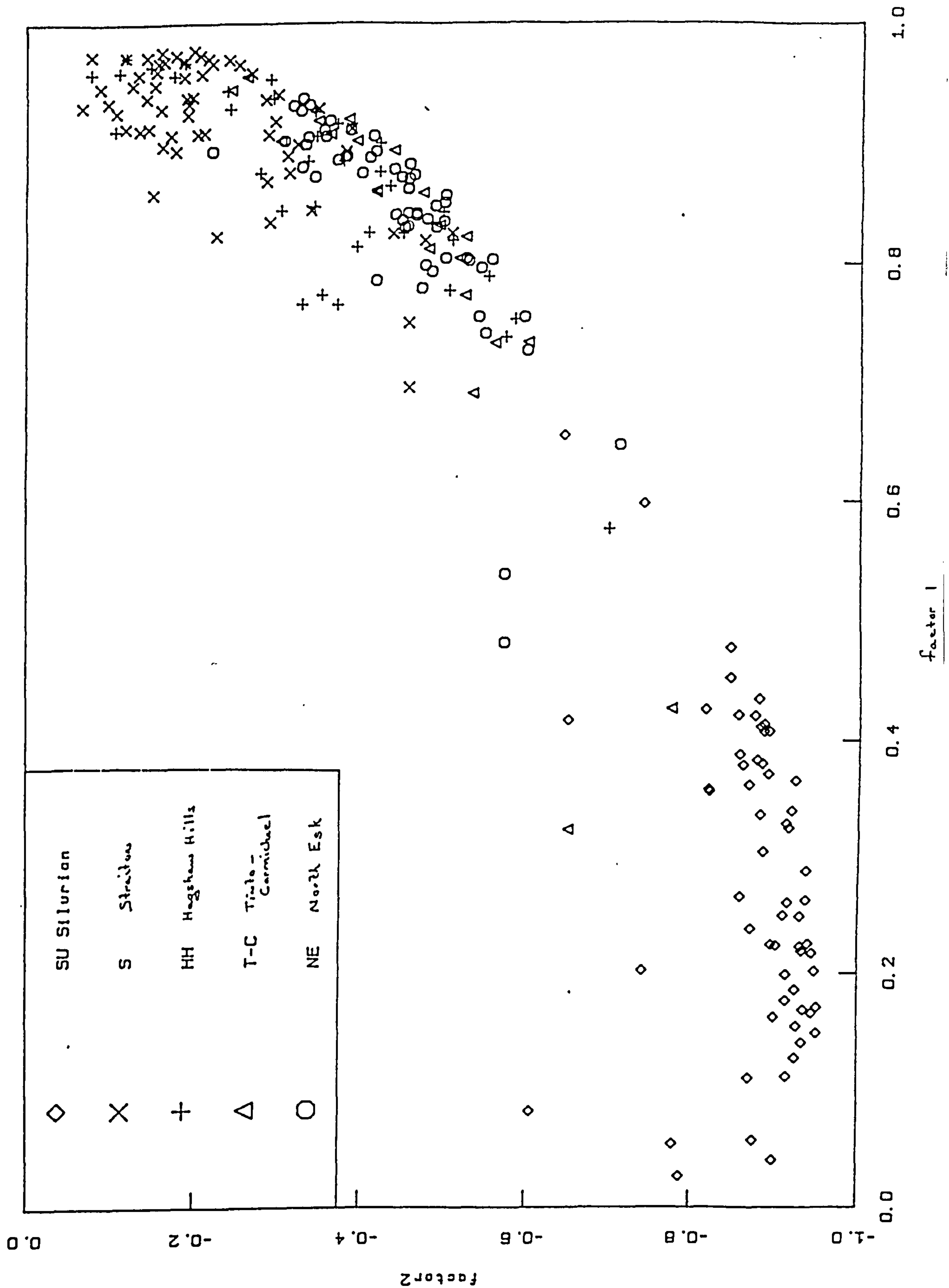


Fig. 4.4.2 Q-mode factor 1 vs factor 2 for Southern Uplands Silurian sediments and Midland Valley sandstone clasts.

Midland Valley-SU Ordovician

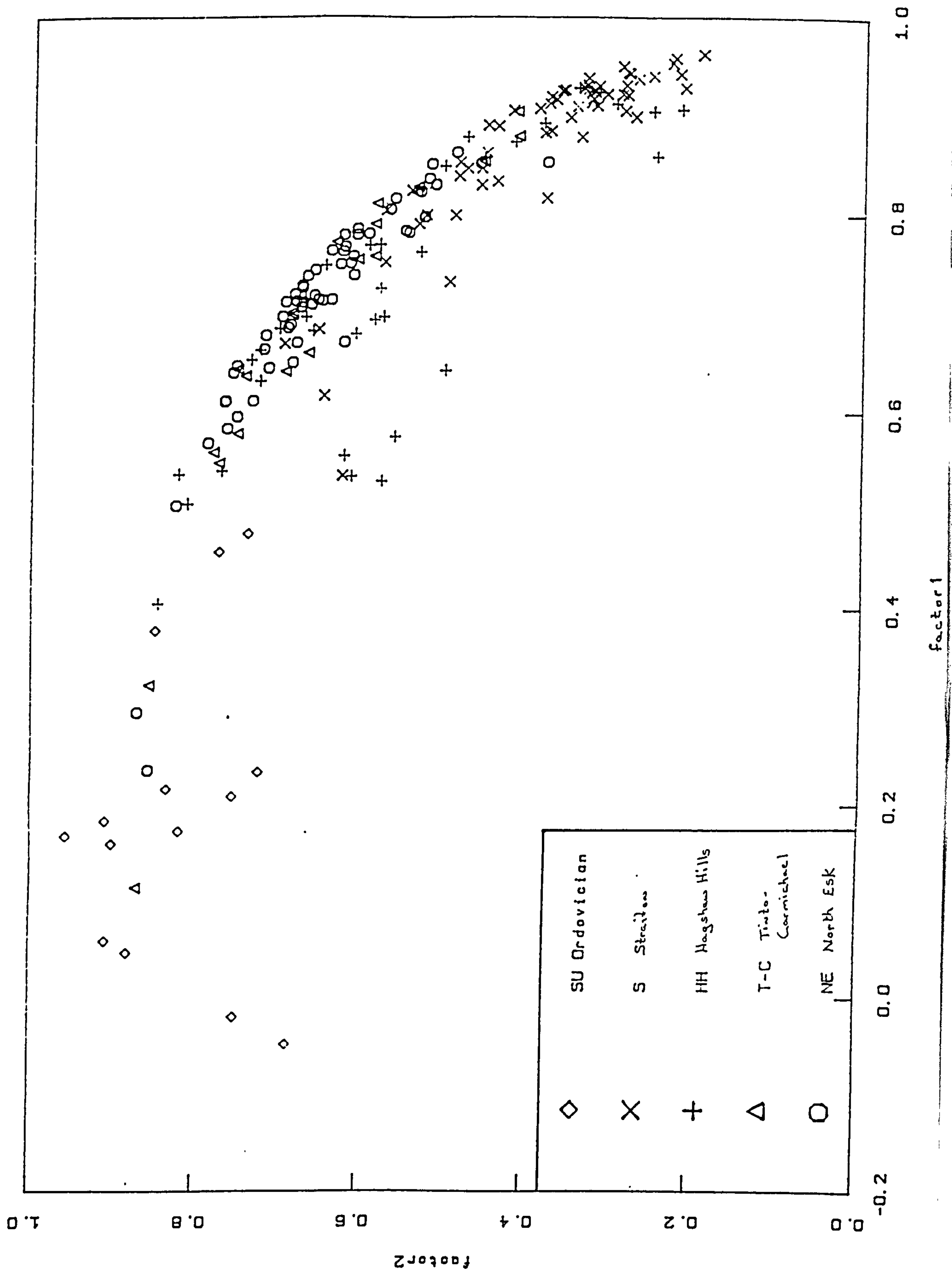
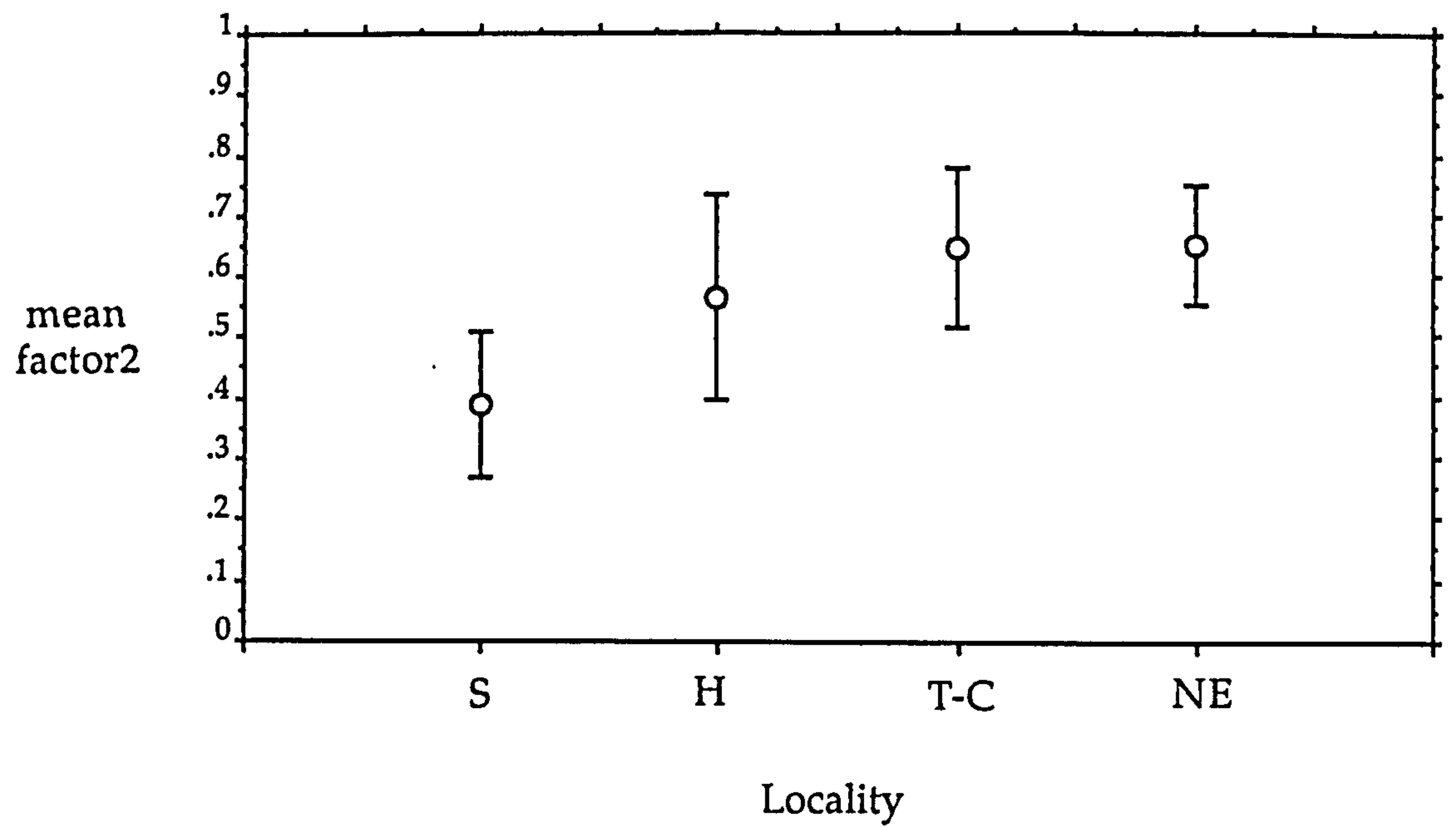


Fig. 4.4.1 Q-mode factor 1 vs factor 2 for Southern Uplands Ordovician sediments and Midland Valley sandstone clasts.

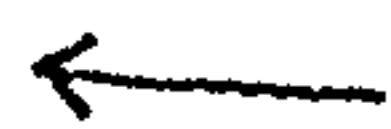


I standard deviation about mean

Fig. 4.4.3. Locality vs. mean value of Factor 2 (from Fig. 4.4.1)
showing the progressive enrichment in feldspar, matrix
and volcanic fragments toward the NE.

Plates

- 4.1 Typical quartz-rich sample from Stration section 2 showing abundant low-grade schist fragments and mica. (x 20)
- 4.2 Relatively mafic-rich sandstone from Hagshaw Hills containing significant proportion of schist rock fragments. (x 20)
- 4.3 Mafic-rich sandstone from Tinto with biotite bearing intermediate volcanic fragment, top right hand corner. (x 20)
- 4.4 Quartz and feldspar rich sample from Carmichael with epidotized acid igneous rock fragment, center. (x 20)
- 4.5 Quartz-rich sample from North esk containing "coarse-grained felsitic" fragments, basic igneous fragments, and metaquartzites. (x 20)
- 4.6 Rutilized feldspar typical of Stration and Hagshaw Hills samples. (x 20)
- 4.7 Deformed felsitic fragment found in both Stration and Hagshaw Hills samples. (x 40)
- 4.8 Veined basic volcanic fragment found in both Straiton and Hagshaw Hills samples. (x 20)
- 4.9 Well rounded tourmaline core with secondary overgrowth from Carmichael. (x 20)



basic
igneous rock
fragments

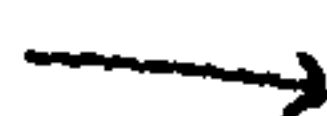


plate 4.1

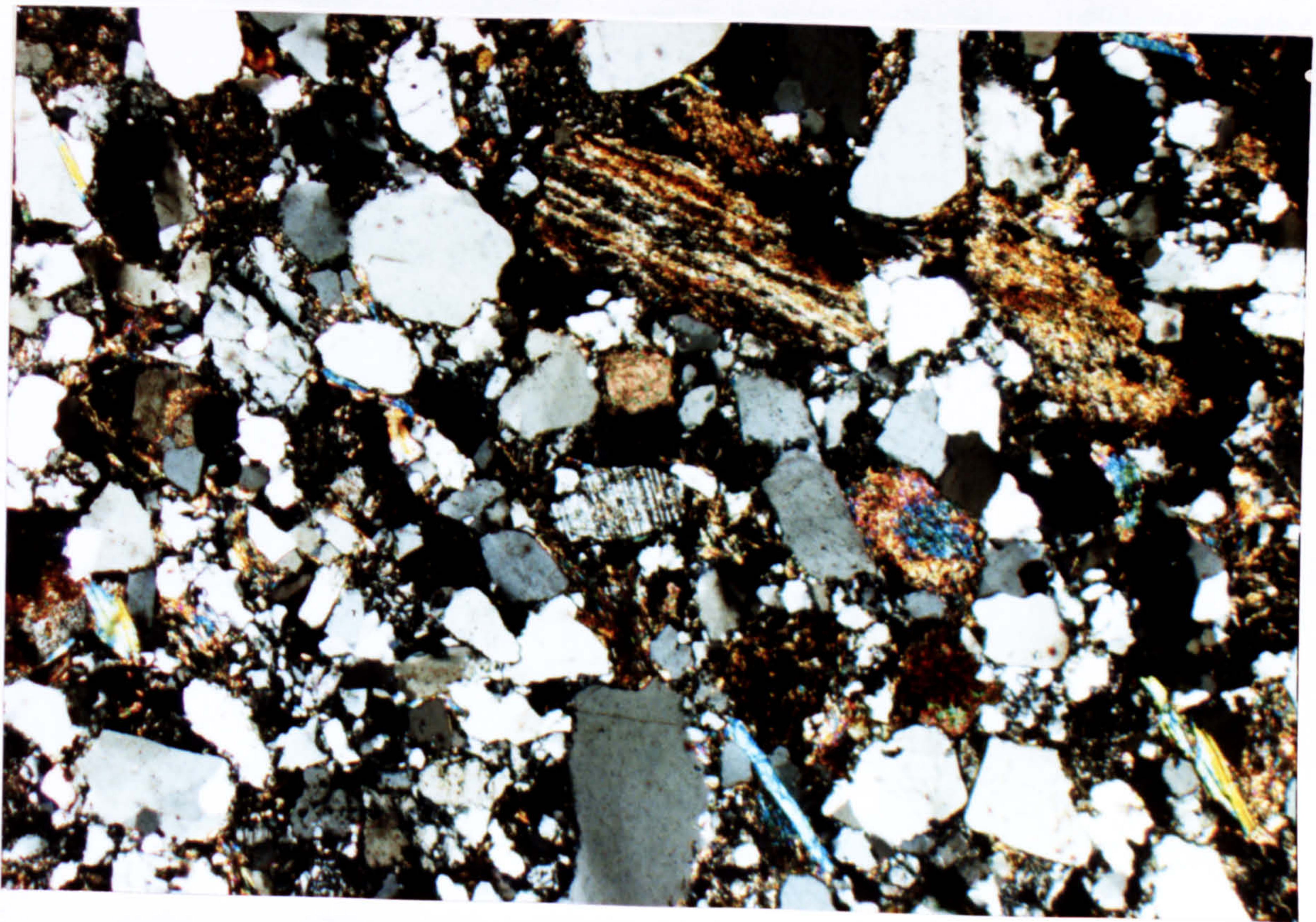


plate 4.2

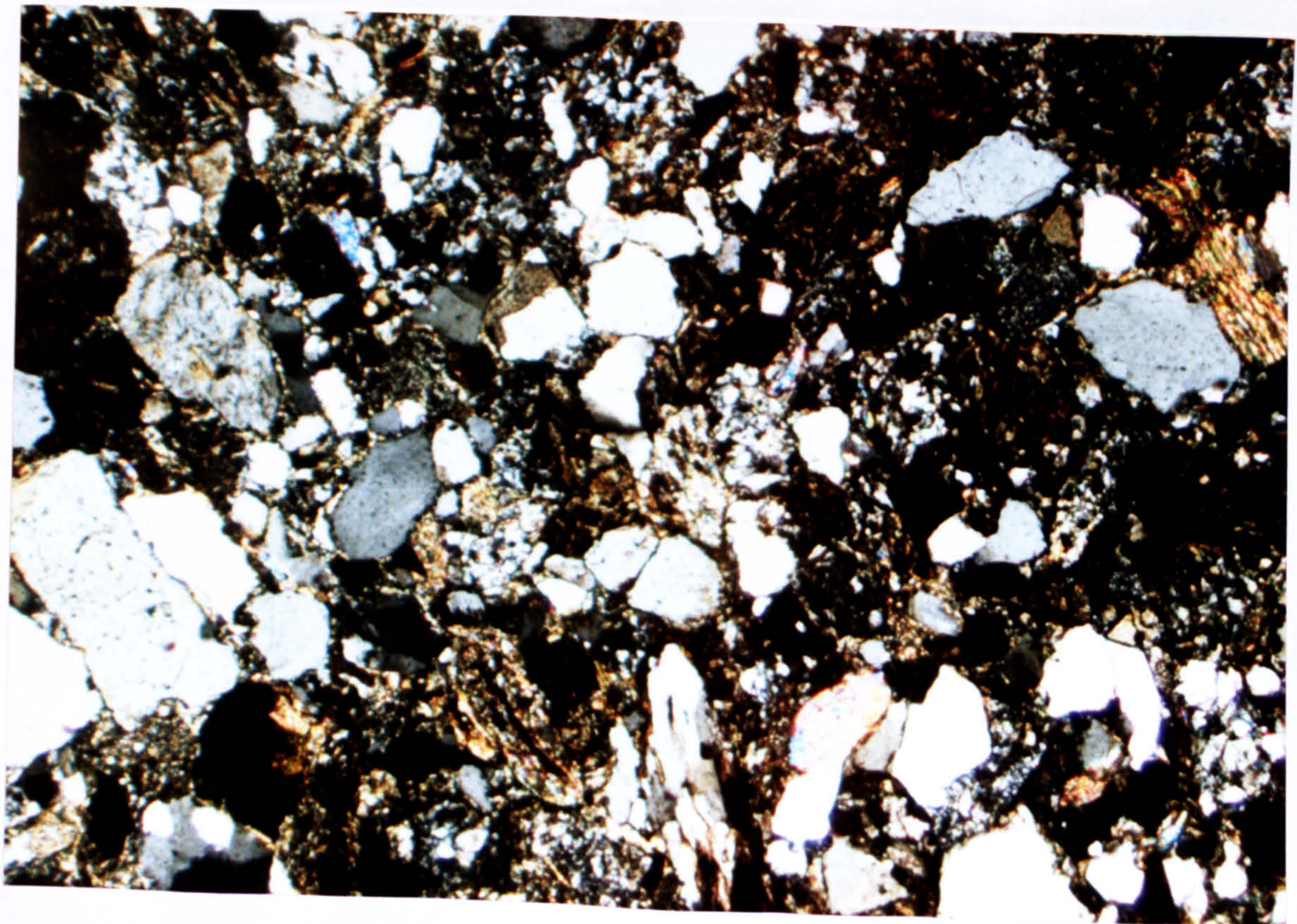


plate 4.1

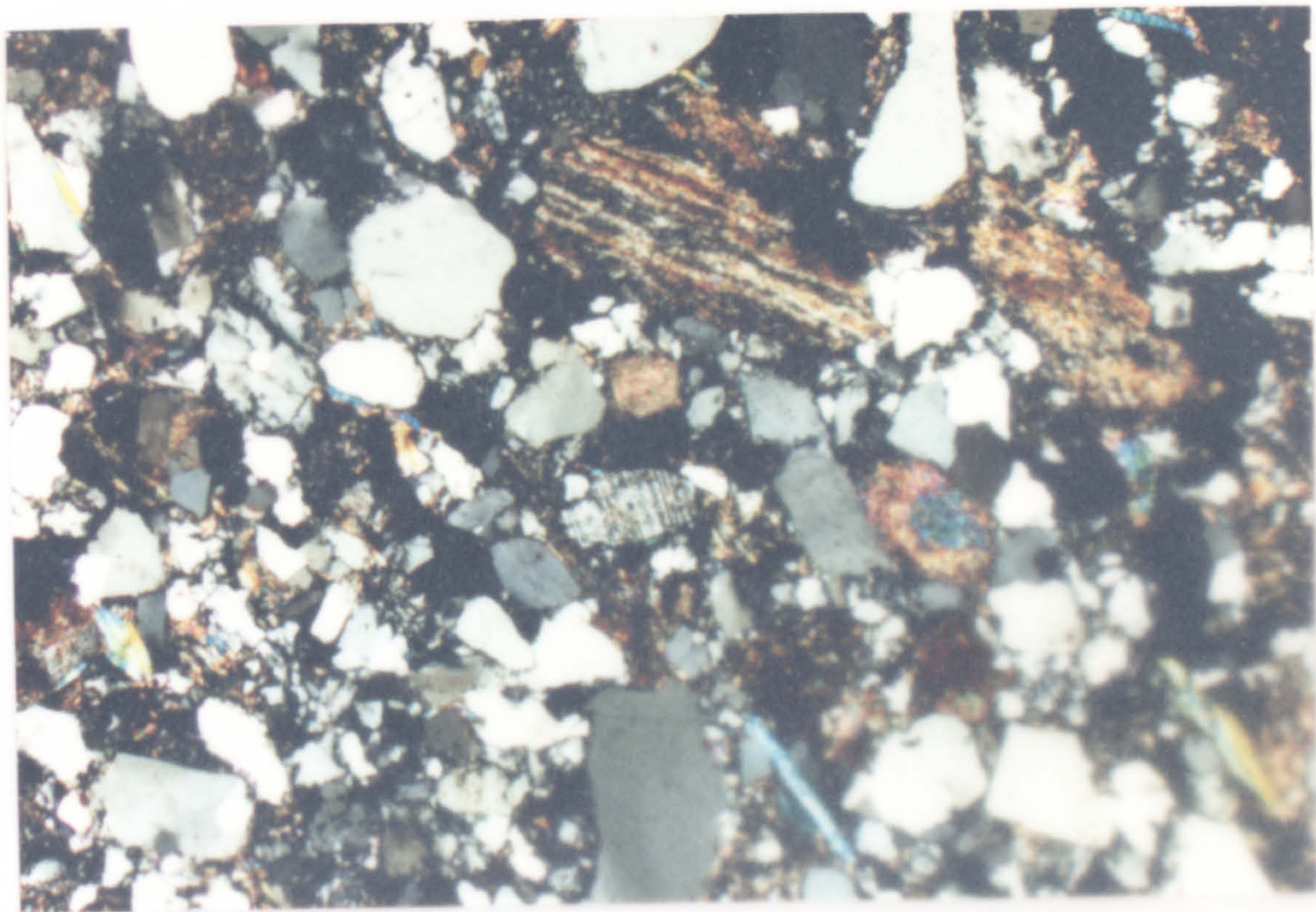
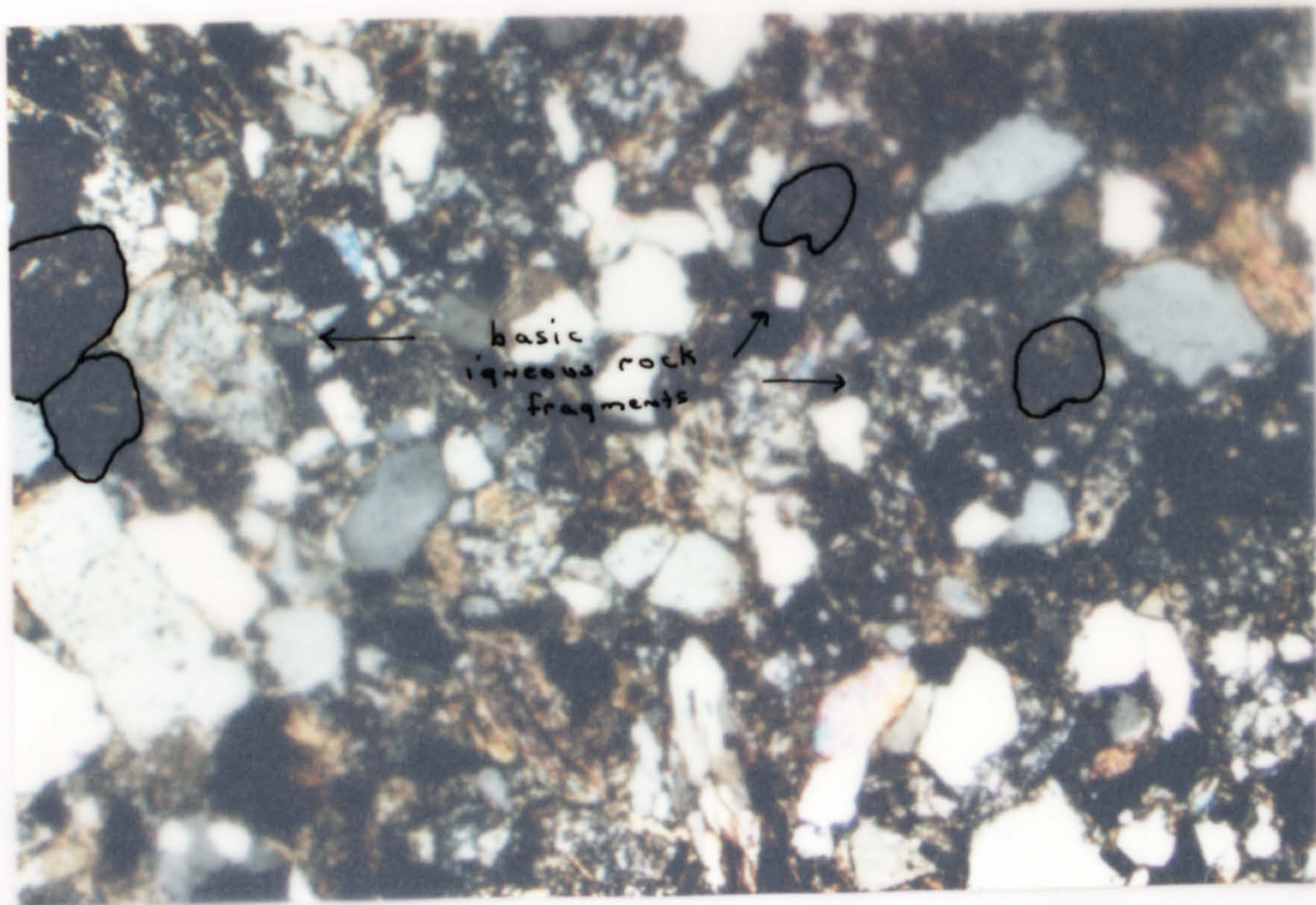


plate 4.2



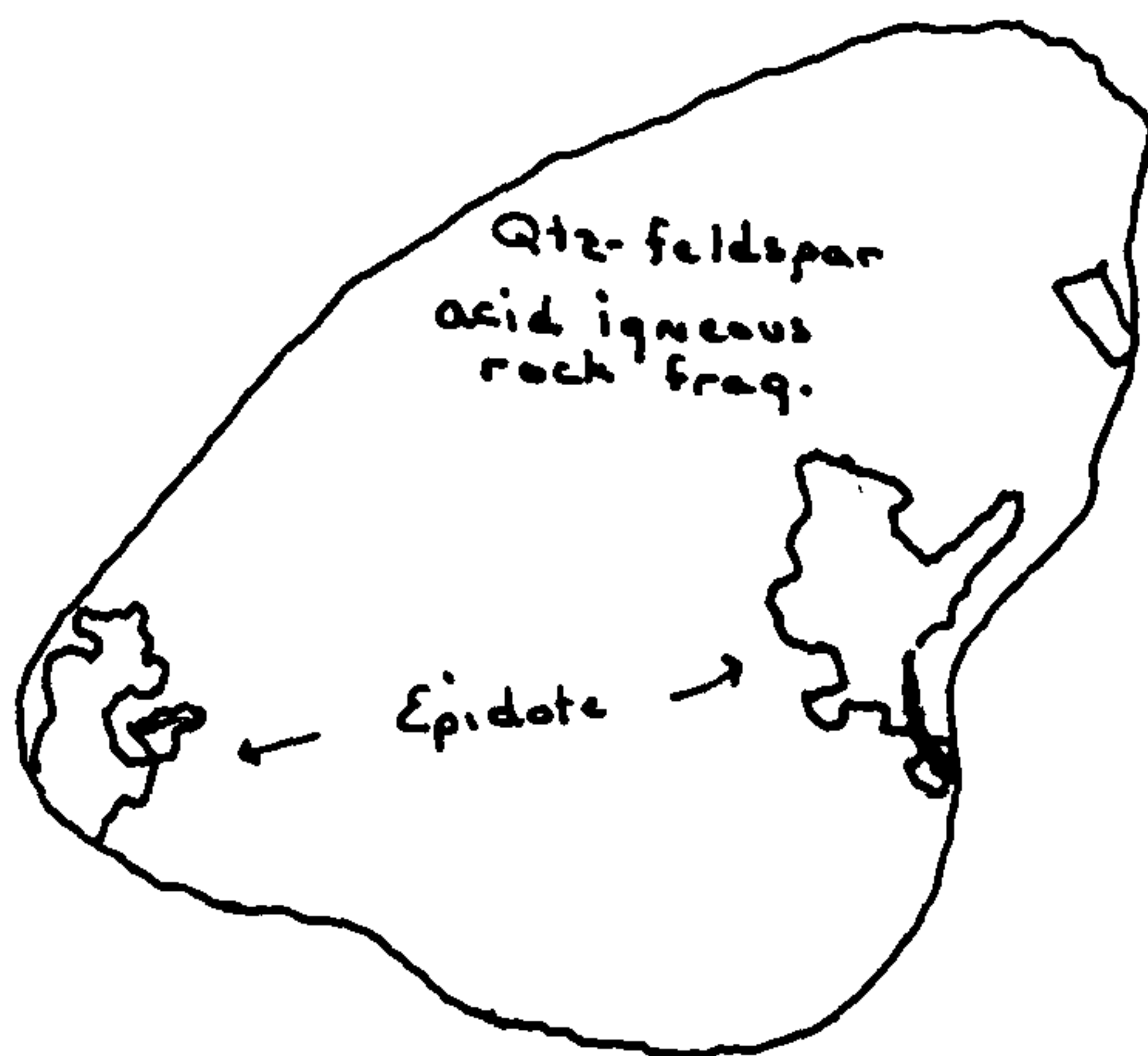
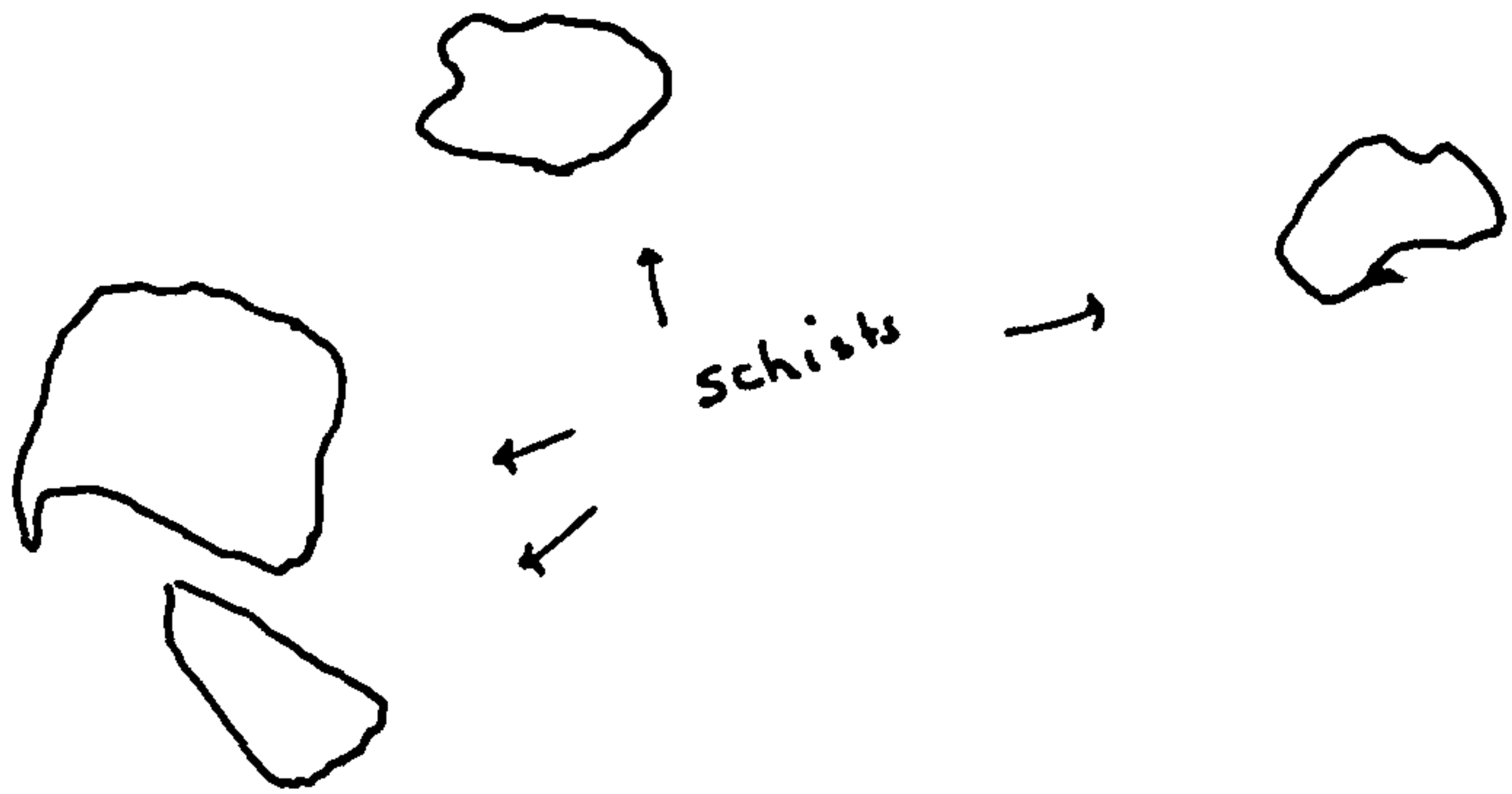


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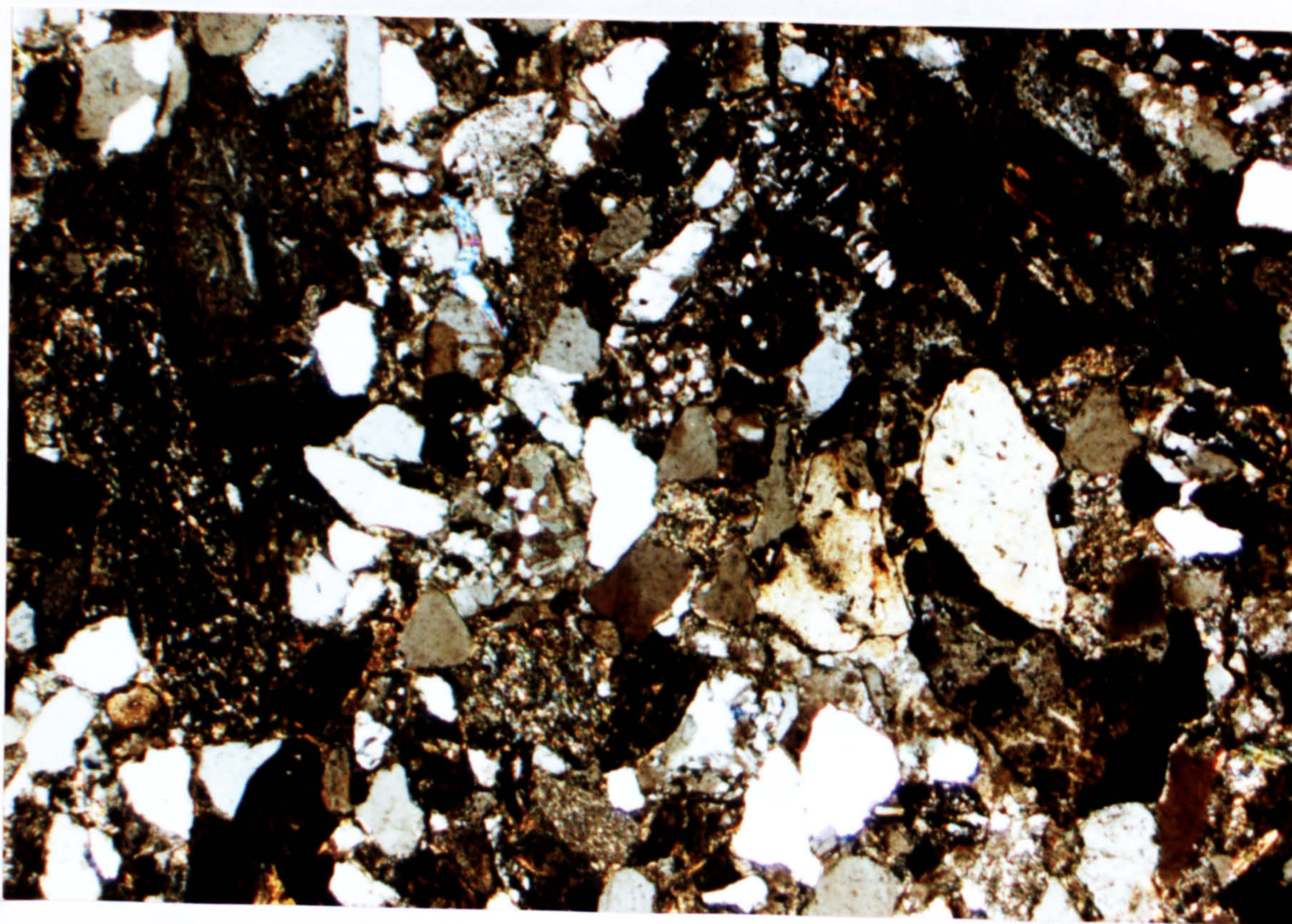


plate 4.4

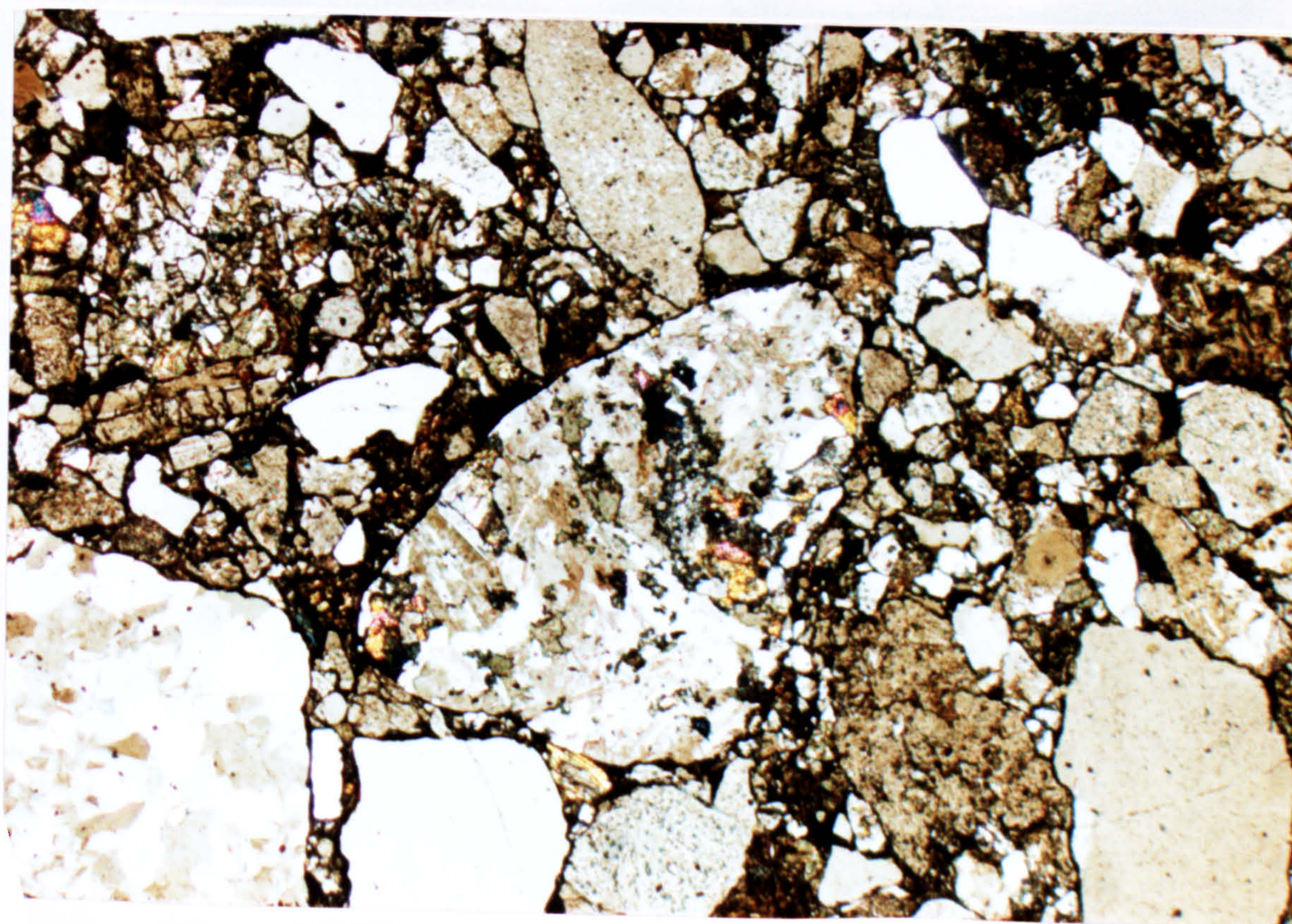


plate 4.3

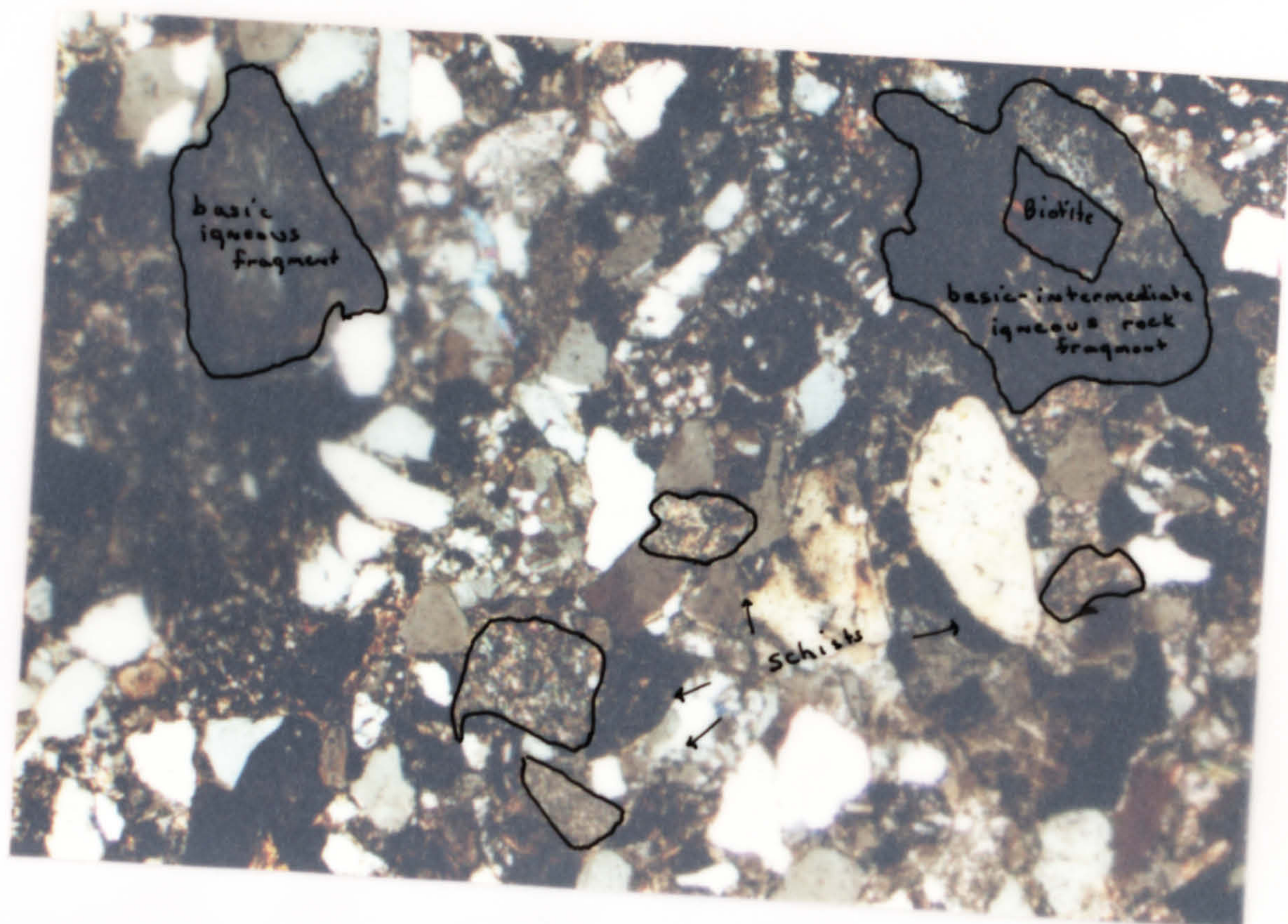
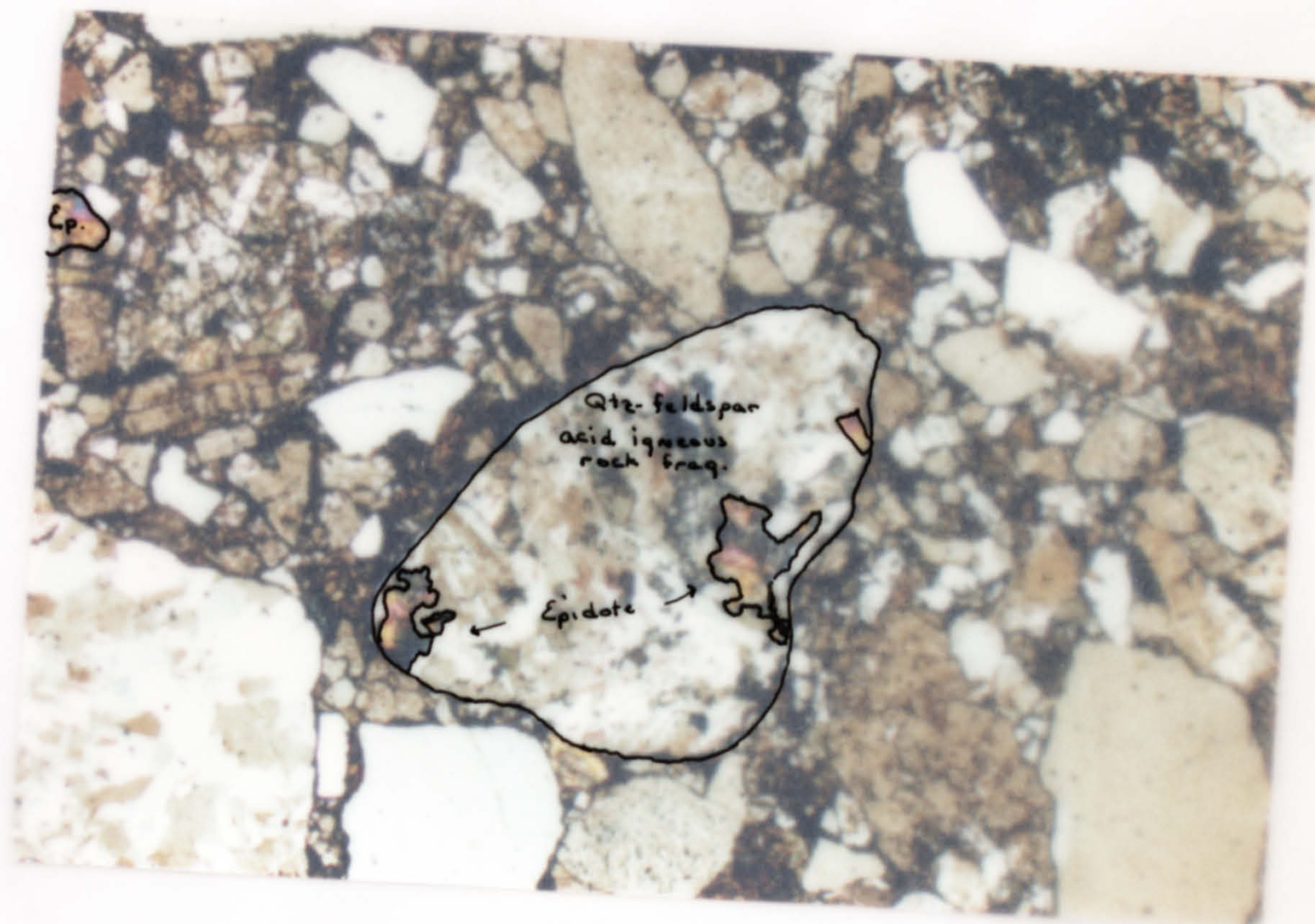


plate 4.4



Felsitic
acid frag.

basic
iq.
frag.

metamorphic
quartzite

basic
iq.
frag.

Felsitic
acid frag.

Coarse
Felsitic
acid
frag.

rutilized
feldspar

plate 4.5

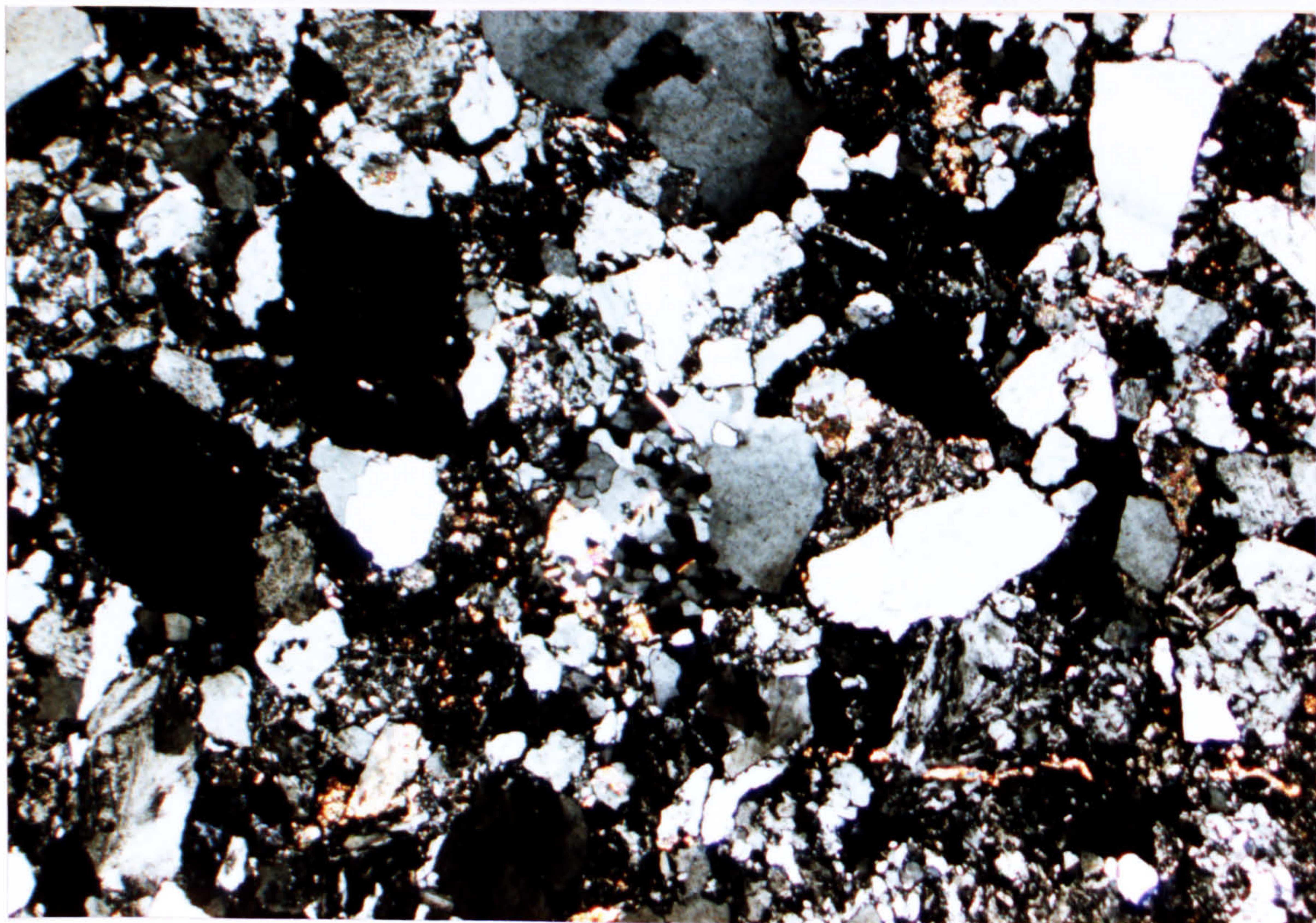


plate 4.6

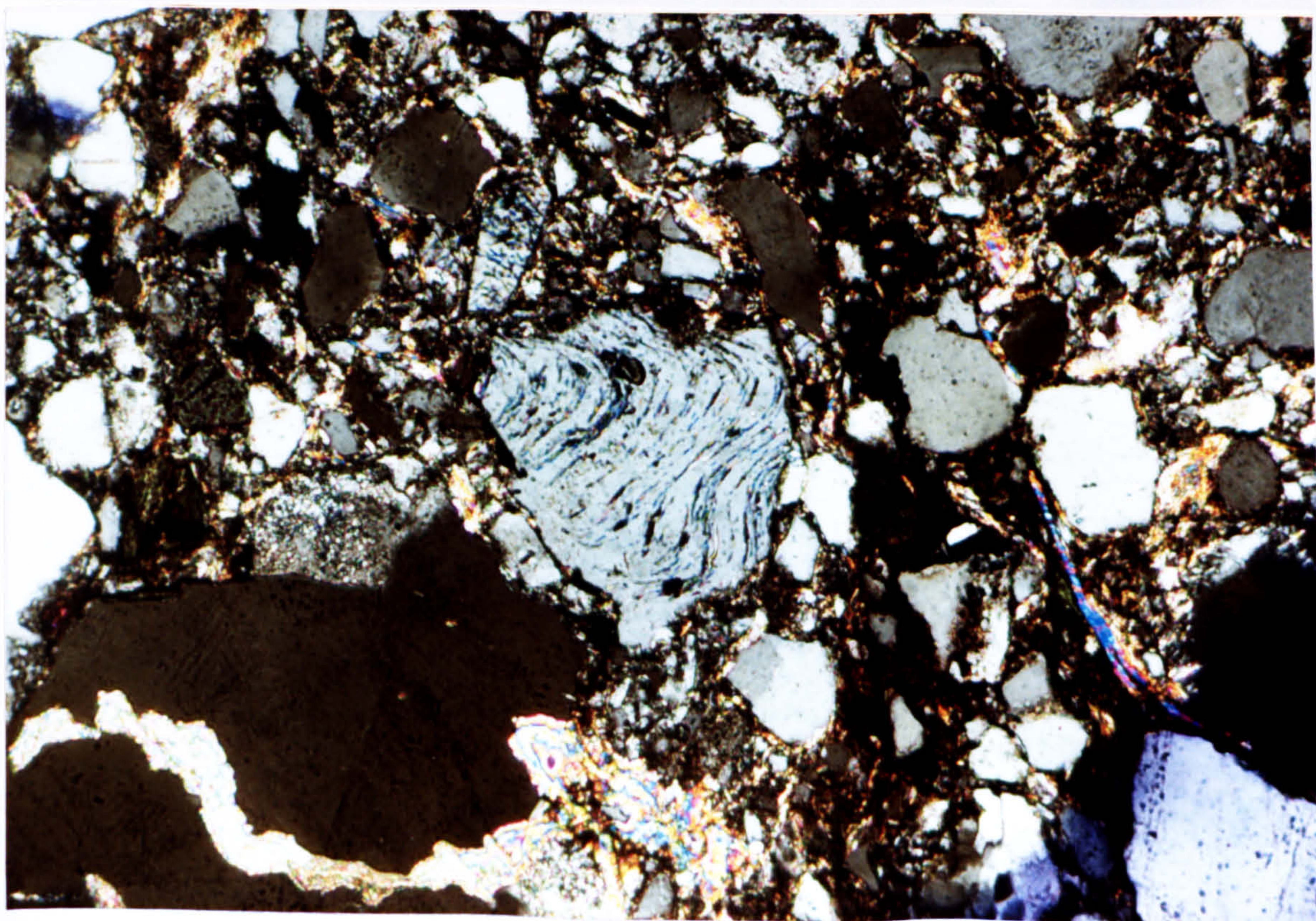


plate 4.5

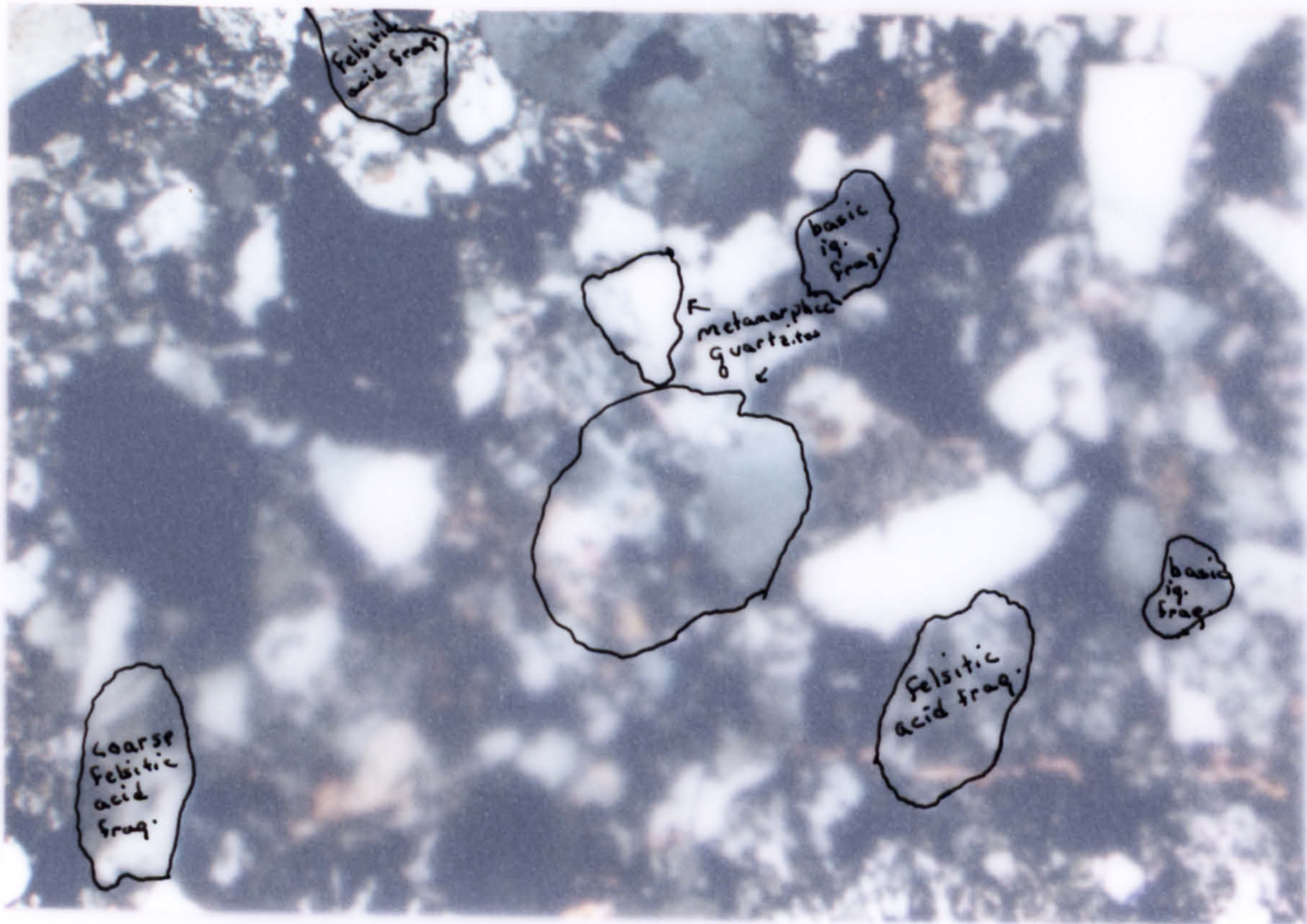
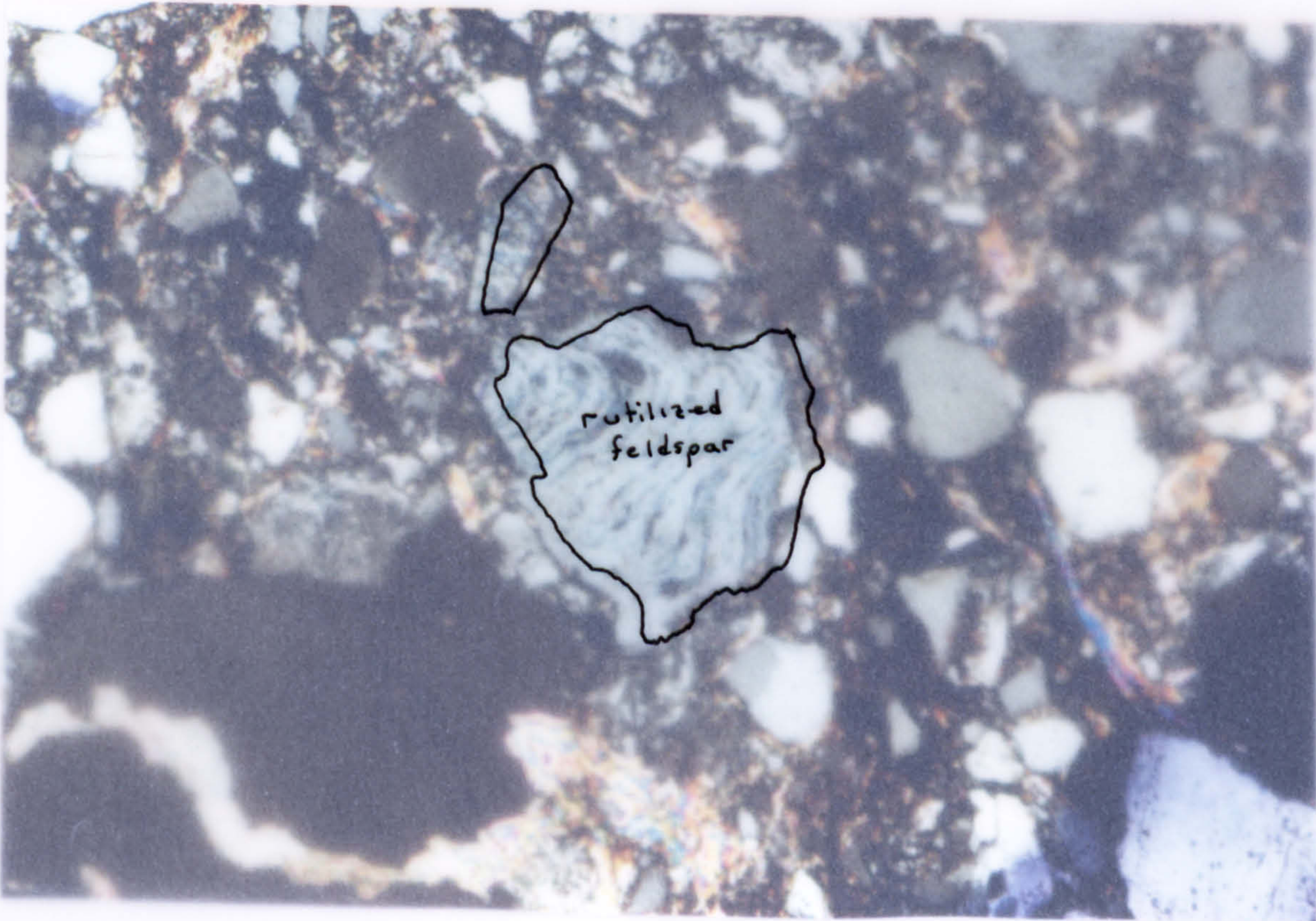


plate 4.6



altered
feldspar

veined
basic
igneous rock
fragment

basic
ig. rock
fragment

plate 4.7

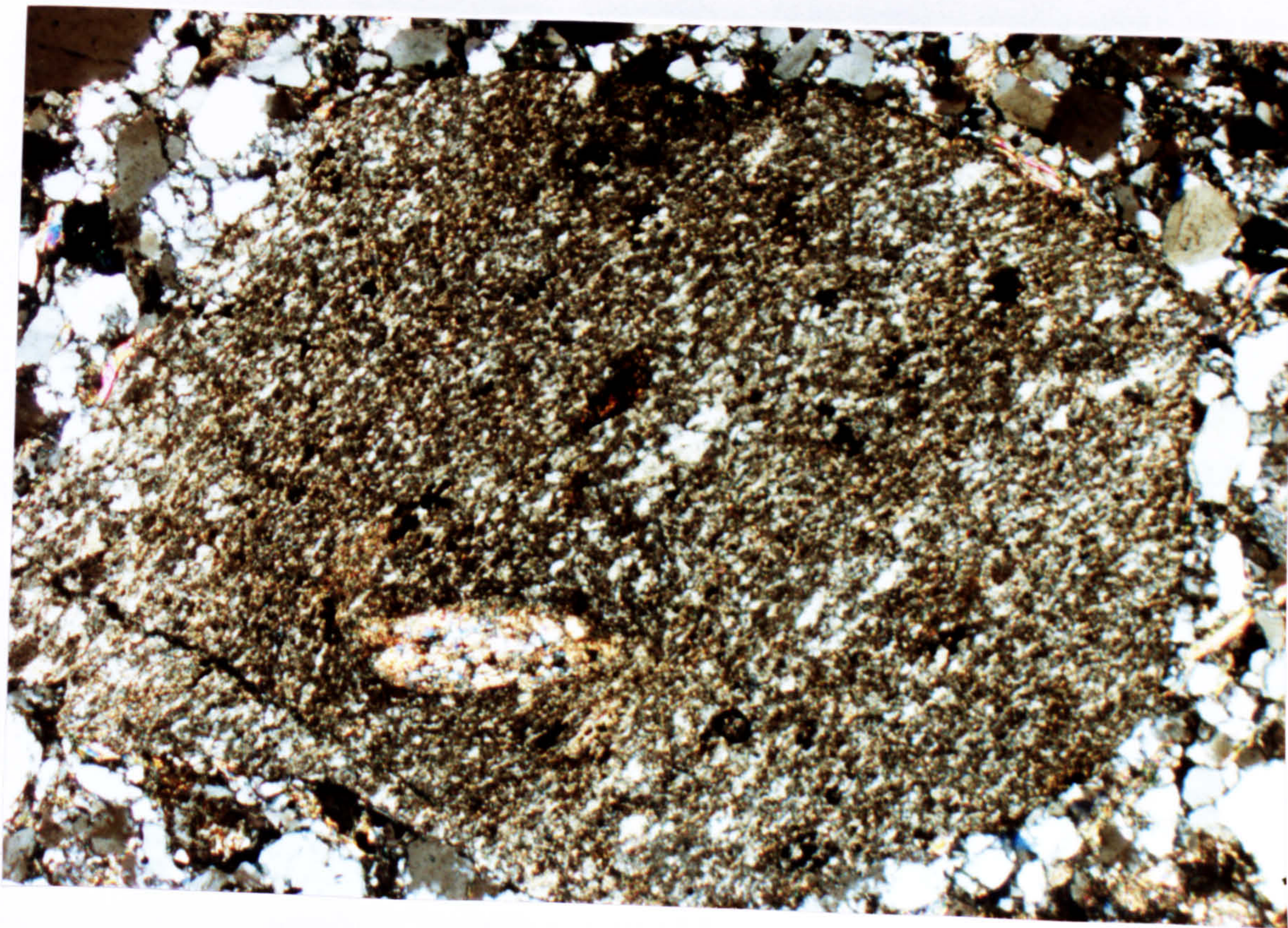


plate 4.8

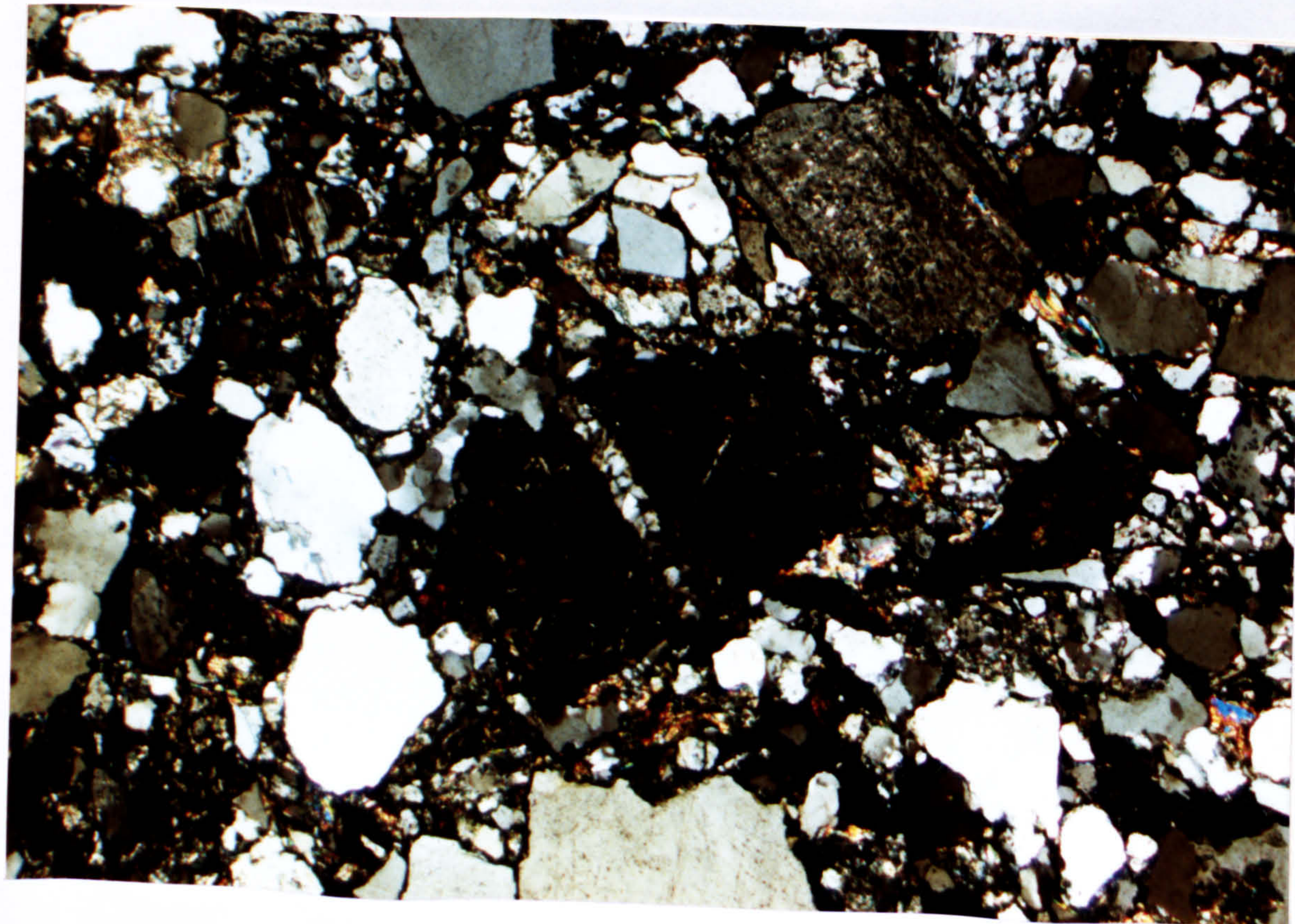


plate 4.7



plate 4.8

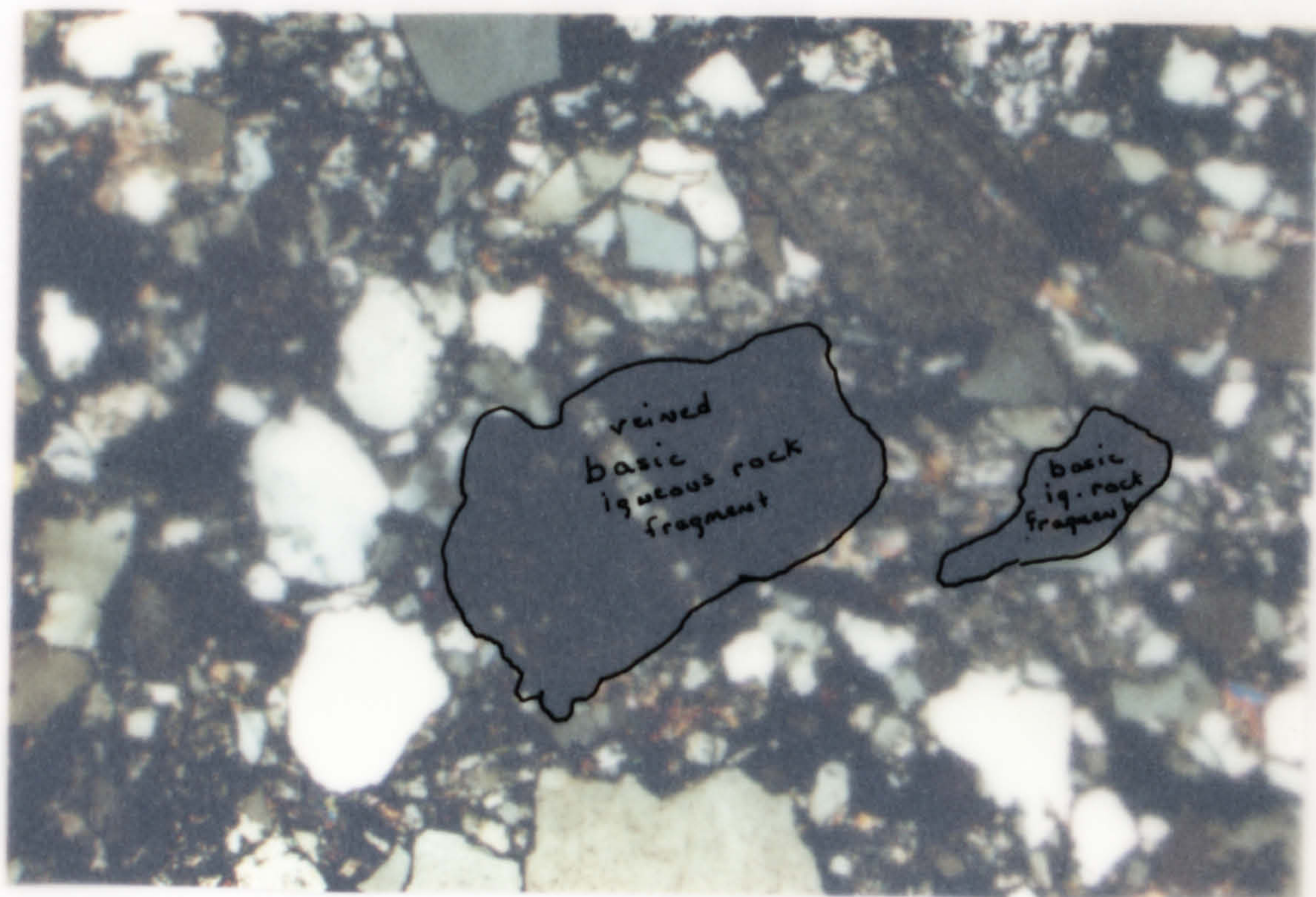
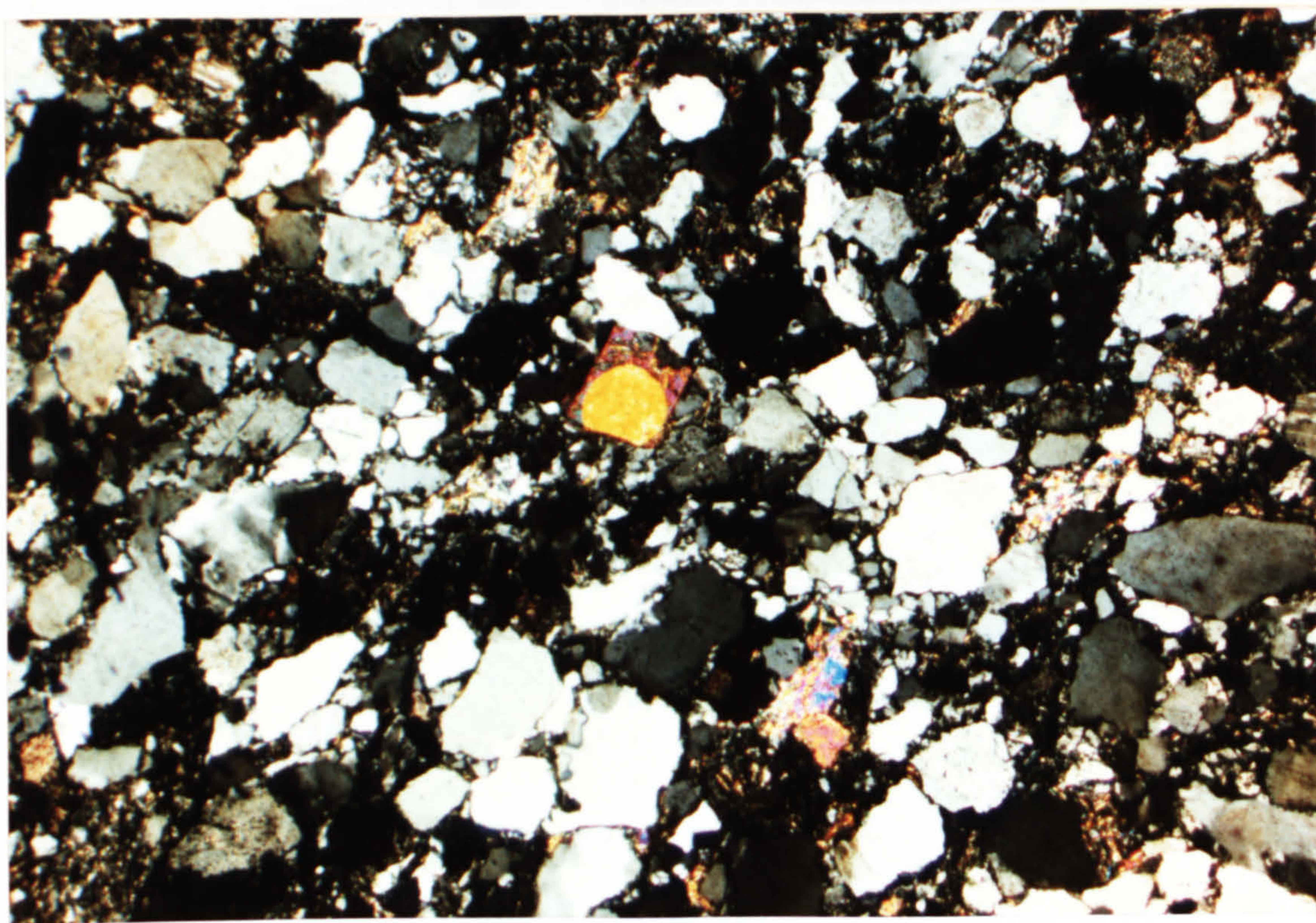


plate 4.9



5.0 Geochemistry of the Greywacke Conglomerate sandstone clasts

Geochemical analysis of 203 collected sandstone clasts are detailed in the following chapter. Major and minor oxides along with trace elements were determined by x-ray fluorescence using the methods of Leake *et al.* (1969) and Harvey *et al.* (1972). The results for individual samples are located in Appendix B.

Before discussing the results it is important to point out that there is a positive correlation between % CaO and % CO₂, (Fig. 5.1), with very few of the samples lying away from a straight line, probably the result of analytical error in the determination of % CO₂ in these samples. It is therefore expected that the majority of CaO is located in calcium carbonate and the individual samples have been recalculated on a carbonate free basis labeled with an asterisk (*). Many of the Straiton samples show a lower gradient than expected if all the CO₂ is associated with calcite and positive correlations between CO₂-Fe₂O₃, -FeO, and -MgO (see sect. 5.3) indicate that siderite and/or dolomite might be important carbonate phases in the Straiton area. Although a significant correlation between CaO and MgO is not discernible in the Straiton sandstones, (Fig. 5.2 a), there is a suggestion that above 2.0% CaO there is an increase in MgO compared to the Hagshaw Hills through to the North Esk samples, (Fig. 5.2 b). All calculations, figures and tables in this chapter use the carbonate free calculations unless otherwise stated.

The geochemical signature of sandstones is a function of source rock composition, weathering, sorting, and post-depositional diagenesis. The ultimate aim in any geochemical analysis of terrigenous sediments is to accurately decipher the interaction of the above variables and determine the effect each has on the present day bulk geochemical composition of the sediments. Only after careful consideration of sedimentary and post-depositional processes which affect the distribution of the elements can a coherent and useful correlation between ancient sediments in varying tectonic regimes be considered.

The objective of this chapter is to:

- 1). determine the geochemical variation between sandstone clasts from the four main exposures of the Greywacke Conglomerate, *i. e.* Straiton (S), Hagshaw Hills (H), Tinto-Carmichael (T-C), and North Esk (NE)
- 2). relate the variation to source rock composition, sedimentary processes and/or diagenesis
- 3). identify using geochemical signatures the tectonic setting of the sedimentary basin in which the sandstones were deposited and

4). compare the geochemistry of the sandstones from the Greywacke Conglomerate with similar clasts found in the Midland Valley and sediments from the Southern Uplands.

5.1 Summary and comparative statistics within the Greywacke Conglomerate.

Mean, standard deviation, and ranges for 13 major and minor oxides and 17 trace elements are presented in Tables (5.1.1-5.1.6). Table (5.1.1) represents the summary statistics for the total 203 sandstone clasts whereas Tables (5.1.2-5.1.6) are the summary statistics for collections from the Straiton (n=72), Hagshaw Hills (n=44), Tinto (n=16), and North Esk (n=64), respectively. A complete treatment of the statistical methods used below is given in Davis (1986).

To establish the likelihood that each area has a single parent population for a specific variable a comparison of the chemical oxides and elements can be made using the Students t-test. Where t given below is compared to the t-distribution, the distribution dependent on sample size which would be expected from randomly sampling a normally distributed population.

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s_e}$$

\bar{X} = mean

s_e = standard error of the mean

and $s_e = s_p \sqrt{1/n_1 + 1/n_2}$

$$s_p = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

n = number of samples

s_p = pooled estimate of the standard deviation (s)

Three assumptions are made when using the t-test of equivalence.

- 1). Both samples were selected at random
- 2). Populations from which the samples were drawn are normally distributed

3). The variances of the two populations are equal

The Greywacke Conglomerate is exceptionally uniform in clast composition. Sandstones form the majority of clasts, with the exception of the Carmichael conglomerates, and would decrease the possibility that clasts were chosen from specific horizons which contain a higher proportion of any one type of sandstone clasts. Care was taken to assure that each clast was randomly selected.

The central limits theorem states that if random samples are collected from any population their means will tend toward a normal distribution. The larger the sample size the more normally the means will be distributed and the second criteria will only be important if the sample size is small. The small number of samples collected from Carmichael (n=7) could introduce a bias into the data. However, the chemical homogeneity of the sandstones, with the exception of 5c1, which does not adversely effect the distribution, and the similarity of the standard deviations to the standard deviations in the remaining areas suggest that a bias in the means has not been introduced from these samples.

The third criteria , equality of variances, can be tested using the F-test. The F-test is based on the probability of obtaining specified ratios of sample variances from a single population. The F-distribution is thus based on randomly selecting two sample populations from a normally distributed parent population and calculating the ratio of all possible pairs of sample variance using:

$$F = \frac{S_1^2}{S_2^2}$$

The ratio obtained from the two sample population in question can then be compared to the values obtained from the F-distribution. This ratio is dependent upon sample size and will vary more from trial to trial if the sample size is small.

As noted above the t-distribution is also affected by the number of observations where the uncertainty introduced by estimating the parent population mean and standard deviation from the sample population gives a wider spread to the distribution when compared to the normal distribution. It follows that the smaller the sample size the larger the uncertainty in the data and the wider the spread of the t-distribution.

Table (5.1.7) shows the t- and F- tests comparative statistics for each oxide and trace element from their respective areas. The values in bold type indicate they are statistically significant at the 95% confidence level for both the t- and the F-tests. It can be seen that very few of the chemical oxides and elements from the Straiton area would be expected to share a similar parent population which gave rise to the Hagshaw Hills, Tinto, and North Esk sandstones.

There is a number of major oxides and trace elements in the Hagshaw Hills, Tinto, and North Esk comparative tests which are significant and would indicate these groups are distinctly similar. Of particular importance is the equivalence of mean % SiO_2 from each of the above areas.

Percent SiO_2 is predominantly free quartz in sandstones and as such is an indicator of textural maturity and source rock composition. However, the majority of the sandstone clasts from the Greywacke Conglomerate are texturally immature (see sect. 4.2) indicating the dominant control on % SiO_2 was source rock composition. Quartz introduced by veining is not an important feature in the sandstones and would negate any substantial change in the % SiO_2 by diagenetic veining. Dissolution of quartz by pressure solution has occurred in some of the samples especially in the matrix-poor, quartz-rich varieties but the loss of SiO_2 must be fairly negligible as it would affect the variance and the test for equivalence would fail. The fact that each of these areas show statistically significant levels of SiO_2 would imply a similar source rock terrain.

When compared with each area Carmichael shows an increase in the number of variables which would be considered to be from a single parent population. However, the relatively few samples from this area has induced a wider spread and therefore larger degree of uncertainty for both the t- and F- distributions giving rise to an increased number of significant values with all areas. The substantial increase in the number of significant values that Carmichael shows with the Hagshaw Hills, Tinto, and North Esk when compared with Straiton indicates that clasts in the Carmichael area are chemically more similar to the first three areas than the latter.

Given the above conclusions and the petrographical results from Chapter 4 the Straiton area is treated as a chemically distinct group from the remaining four areas. A comparison diagram of the major oxide chemical means between the Straiton area and the Hagshaw Hills, Tinto, Carmichael, and North Esk is given in Fig. (5.1.1). Straiton is enriched in P_2O_5 and slightly enriched in both SiO_2 and K_2O , relative to the other areas. A comparison diagram of the trace element means is given in Fig. (5.1.2), where the Straiton samples are

depleted in trace elements associated with mafic minerals.

5.2. Chemical classification of the sandstone clasts.

Pettijohn *et al.* (1972) classifies sandstones by combining both the textural and mineralogical attributes using the ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{K}_2\text{O}$. An increase in the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ reflects a change from al-rich silicates and clays (immature) to quartz dominated (mature) sandstones. The ratio $\text{Na}_2\text{O}/\text{K}_2\text{O}$ distinguishes plagioclase-rich sediments from orthoclase-rich sediments. The majority of sandstones from the Greywacke Conglomerate classified by the above method fall into the lithic arenite category, (Fig. 5.2.1). This corresponds to an enrichment in SiO_2 when compared to the typical greywacke, but the relatively low value of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ also shows the chemical immaturity of the sandstone clasts. A number of the Straiton samples fall into the arkose field reflecting the high K_2O values relative to Na_2O associated with these sediments.

A distinction between greywackes and arkoses is commonly made by the ratio of $\text{Na}_2\text{O}/\text{K}_2\text{O}$. Greywackes have high Na_2O values relating to the high proportion of albite over calcium rich plagioclase. As noted in the petrographic examination of the sandstones, irregular patches of carbonate within the feldspar and matrix suggest the albitization of original ca-plagioclase. Fig. (5.2.2) shows a clear distinction between the more sodic-rich sandstones from the Hagshaw Hills, Tinto, Carmichael and North Esk and the potassium-rich Straiton sandstones. Feldspar percentages do not increase in the Straiton sandstones and instead decrease compared to the other areas. Clearly, the Straiton sandstone clasts are not arkoses in the classical sense, instead the high proportion of K_2O reflects the high percentage of muscovite bearing metamorphics found in these sandstones.

5.3 Oxide and trace element correlations.

The standardized linear relationship between two variables can be expressed by the correlation coefficient (r), where r is the ratio of the covariance to the product of the standard deviations.

$$r = \frac{\text{COV}_{ik}}{S_i S_k} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\left| \sum_{i=1}^n (x_i - \bar{x})^2 \right|^{1/2} \cdot \left| \sum_{i=1}^n (y_i - \bar{y})^2 \right|^{1/2}}$$

The covariance may not exceed the product of the standard deviations of the two variables, thus (r) has a range between ± 1 . To test the significance of r at a specified confidence level the t-test expressed as:

$$t = \frac{r \cdot \sqrt{n - 2}}{\sqrt{1 - r^2}}$$

was used.

The t-test is used to test the null hypothesis that r does not show a statistical departure from 0, *i.e.* correlations are absent between the two variables. The above equation may be solved for r , given a particular confidence level and sample size.

The correlation coefficient is adversely affected by a number of factors which include:

1). Non-normality in the distribution of the variables. Most statistical tests require that the variables show a normal distribution.

2). The 'closed array' (Chayes, 1971). The 'closed array' arises where the sum of the variables on an individual sample is constant. The variables themselves represent a percentage of the whole and therefore an increase in one variable, *e.g.* SiO_2 in geochemical analysis, occurs at the expense of the other variables. Induced negative correlations will occur and give rise to spurious significant correlations. To date, there is no universally acceptable method for evaluating the significant inter-correlations between variables in a 'closed array'.

3). Induced correlations may result from differences in variances caused by different units of measurement, the major and trace element constituents.

4). 'Rogue points' which lie outside the main clustering of data can cause a specific variable to correlate with only one member of the group.

Tables (5.3.1-5.3.2) contain the correlation matrices for the Straiton and the H-T-C-NE, respectively. Only the significant values of r at or above 95 % confidence level have been included. Ahrens (1954a,1954b) showed that most of the trace elements follow a lognormal distribution. The correlation matrices were therefore based on the \log_{10} of the original data. The \log of 0 is undefined and all variables containing 0 were given a value of 1 in the original data set. The most obvious consequence of the factors effecting the correlation matrix is the negative correlation between most of the variables and SiO_2 . The absence of negative correlations in the remaining variables is both a function of the chemical maturity of the sandstones and the wide distribution of the elements in a number of minerals.

5.3.1 Intercorrelation and associations of trace element and major oxide variables.

Major variations in sandstone geochemistry can be used to infer: i). changes in source rock composition corresponding to different tectonic setting, ii). maturity indexes relating to

fractionation of the sediments during transportation and, iii). degree of alteration during diagenesis. The use of trace elements in determining potential source terrains is limited unless the location of these elements in detrital phases and influence of diagenetic changes is known. Correlations within and between the major oxides and trace elements is a function of the crystal chemistry of the elements. As such the correlations can be used to infer the location of elements in specific minerals or dual location of the elements in various mineral phases.

Niggli numbers have been used by Van de Kamp *et al.* (1976) and Van de Kamp and Leake (1985) in geochemical provenance studies of unconsolidated sands and sandstones. As pointed out by the authors Niggli numbers eliminate the effect of the 'closed array' where quartz (predominately SiO_2) is the dominate mineral in sandstones. Niggli values are based on the molecular content of the elements and are thus independent of the value of SiO_2 . The Niggli values are determined using the following: Al_2O_3 is (al^\wedge), $\text{K}_2\text{O} + \text{Na}_2\text{O}$ (alk^\wedge), $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO} + \text{MnO}$ (fm^\wedge), K_2O (k^\wedge), TiO_2 (ti^\wedge), SiO_2 (si^\wedge) and $\text{MgO}/(\text{FeO} + \text{MgO} + 2\text{Fe}_2\text{O}_3 + \text{MnO})$ (mg^\wedge). One of the most useful calculations using Niggli numbers is ($\text{al}^\wedge - \text{alk}^\wedge$). The 'excess' aluminum after subtracting the aluminum in alkali feldspars will be located mainly in sheet silicates and anorthite.

The correlations in Tables 5.3.1 and 5.3.2 are used in conjunction with the niggli numbers in identifying: i). the mineral location of the elements from both the H-T-C-NE and Straiton areas, ii). the variations between the two areas and iii). the usefulness of specific elements as provenance indicators. All the following correlations are positive unless otherwise stated.

$\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Ba}-\text{Rb}-\text{Sr}$

The alkali metals K and Na are expected to be located in feldspar, clay minerals and muscovite. Fig. (5.3.1 a) shows a clear positive trend for k^\wedge vs $\text{al}^\wedge - \text{alk}^\wedge$ with displacement to higher $\text{al}^\wedge - \text{alk}^\wedge$ values for the Straiton sandstone clasts. X-ray diffraction studies (see. Fig. 4.1.1) show chlorite and muscovite to be the only sheet silicates in the sandstones, true clay minerals are negligible, indicating that in the Straiton area the 'excess' aluminum is associated mainly in muscovites. Van de Kamp and Leake (1985) give typical values of > 30 $\text{al}^\wedge - \text{alk}^\wedge$ for shales and clay-rich rocks. High $\text{al}^\wedge - \text{alk}^\wedge$ values in the Straiton sandstones reflect the very high percentage of muscovite as detrital flakes and in metamorphic fragments recorded in these sandstones.

An expansion of Fig. (5.3.1 a) at lower $\text{al}^\wedge - \text{alk}^\wedge$ for the H-T-C-NE is shown in Figs. (5.3.1 b-d). A well defined positive trend in the Hagshaw Hills area is in contrast to the Tinto-Carmichael and North Esk areas. The correlation indicates that like the Straiton

sandstones the 'excess' aluminum is located in muscovites, the Hagshaw Hills having a lower percentage of muscovite than the Straiton area. In the North Esk, the majority of samples below 0.40 k^{\wedge} are closely clustered but samples $> 0.40 k^{\wedge}$ show a good positive correlation, these being more closely related to the Straiton and Hagshaw Hills samples. In the Tinto-Carmichael and majority of the North Esk samples the 'excess' aluminum is probably widely distributed in both chlorites and muscovites.

CaO is negligible in all the sandstones after removal of carbonate suggesting that plagioclase feldspar is dominantly if not exclusively albitic in composition. Microprobe analysis on randomly selected twinned plagioclase grains and feldspar phenocrysts in the volcanic fragments in a sample taken from the Hagshaw Hills is given in Fig. (5.3.2). All but two plot at $< 4\%$ An, the upper limit of pure albite used by Maynard (1984).

Sr^{+2} is intermediate in size between Ca^{+2} and K^{+} . Sr easily substitutes into both plagioclase feldspar and k-feldspar but does not favour the 12-fold coordination of K^{+} in mica preferring the 8 and 9-fold coordination of Ca^{+2} and K^{+} in feldspar. A high positive correlation between Sr and Na_2O and a low correlation between Sr and K_2O in the H-T-C-NE sandstones would suggest the sandstones are depleted in K-feldspar relative to plagioclase and the majority of Sr is located in Na-plagioclase feldspar.

It is not clear whether Sr abundances are affected by anorthite content. Data presented by Stueber (1978) shows no clear relationship between Sr and Ca content in plagioclase feldspar and is therefore not possible to use Sr content to ascertain original plagioclase feldspar composition. The presence of basic igneous rock fragments and high correlation of Na_2O with Sr strongly suggests higher anorthite content in the original detrital plagioclase with little loss of Sr during diagenetic substitution of Na for Ca. A relatively high correlation between P_2O_5 and Sr indicates that Sr has substituted for Ca in the apatites.

In contrast to the above sandstones, the Straiton sandstones show a marked decrease in correlation between sr and Na_2O . The absence of a correlation between Na_2O and Al_2O_3 and high correlation between K_2O and Al_2O_3 show the Straiton sandstones are depleted in plagioclase, the aluminum being located in muscovites and k-feldspar.

Sr values do not increase in the Straiton sandstones with increasing CaO, (Fig. 5.3.3), with only a slight increase in Sr for the highest percentage of carbonate recorded (c. 14%), and indicate that most of the Sr is in the original detrital fraction. There is a very poor negative trend between Sr and $al^{\wedge}-alk^{\wedge}$ (Fig. 5.3.4) where r substitution in muscovites, which dominate the sheet silicates in these sandstones, is very low. Sr has low correlations with a

number of elements and oxides but shows the highest correlations with P_2O_5 where it is probably located in apatites and widely distributed in a number of minerals.

Ba^{+2} and K^+ have identical ionic radius and high abundances of Ba occurs in both K-feldspar and muscovite. However, Ba prefers the structure of k-feldspar to muscovite. A very strong correlation is present between K_2O and Ba in the Straiton sandstones, (Table 5.3.2). There is no clear negative trend between Ba and $al^{+}-alk^{+}$ (Fig. 5.3.5 a), a situation expected if all the Ba were substituting for K in orthoclase feldspar. In the Straiton sandstones, the substitution of Ba for K thus occurs in both muscovite and k-feldspar. There is a marked decrease in correlation between Ba and K_2O in the H-T-C-NE, again indicating an overall depletion of K-feldspar in these sandstones compared with the Straiton sandstones. Fig. (5.3.6 a-c) shows there is considerable variation in the correlation of Ba and K_2O between these sandstones. In the T-C-H-NE Ba shows a positive correlation with K_2O but there is considerable scatter.

Plots of $al^{+}-alk^{+}$ verses Ba (Fig. 5.3.5 b-d) reveal a negative trend for the majority of the T-C samples and no clear trends for the Hagshaw Hills and North Esk samples. The T-C samples are unique in that Ba is mainly associated with K-feldspar.

Rb^{+} has a similar ionic radius to K^{+} and high correlations between Rb and K_2O occur in all the sandstones, (Table 5.3.1, Fig. 5.3.7 a-d). Rb has a slightly larger ionic radius than K^{+} and favours the larger sites available in the 12-fold coordinated micas compared to the 9-fold coordinated feldspars. In contrast to the Hagshaw Hills area, which has a well defined positive trend for Rb vs $al^{+}-alk^{+}$ (Fig. 5.3.8 b), there is no well defined trends in the Straiton (Fig. 5.3.8 a) or the T-C-NE areas (Fig. 5.3.8 c-d).

In summary, high correlations between rb and ba with K_2O in the Straiton sandstones show that Rb and Ba are associated with the K-bearing minerals muscovite and orthoclase. A high positive correlation between k^{+} and $al^{+}-alk^{+}$ show the sheet silicates are dominantly muscovites and a significant proportion of k-feldspar is present as evidenced from the absence of a strong positive correlation between Rb and $al^{+}-alk^{+}$ or negative correlation between Ba and $al^{+}-alk^{+}$.

In general, the H-T-C-NE sandstones are enriched in plagioclase (albite) and depleted in muscovite and k-feldspar compared to the Straiton sandstones. However, in the T-C sandstones a positive correlation between K_2O and Ba along with a negative correlation between Ba and $al^{+}-alk^{+}$ indicates that k-feldspar is an important constituent in these sandstones and dominant over muscovite. The reduced positive correlations between Ba and K_2O in the H-NE sandstones indicate ba may be entering Ca-bearing minerals not present in

the T-C or S sandstones. The lack of correlation between Ba and Na₂O suggest variations in plagioclase abundances could not account for the scatter. The Hagshaw Hills sandstones are enriched in muscovite relative to the T-C-NE which do not show positive trends between k⁺ and al⁺-alk⁺, the 'excess' aluminum probably widely distributed among chlorites and muscovites. A decrease in k-feldspar in the Hagshaw Hills relative to the Straiton sandstones is indicated by the positive correlation between Rb and al⁺-alk⁺ in the Hagshaw Hills samples.

MgO-FeO-Fe₂O₃-TiO₂ and associated trace elements

A plot of fm⁺ against si⁺ shows a well defined negative trend for the Straiton sandstones not developed in the H-T-C-NE sandstones (Fig. 5.3.9). Sands derived mainly from igneous rocks show a decrease in ferromagnesium oxides with increasing quartz associated with fractionation of the igneous body. The absence of this trend in the H-T-C-NE sandstones, which have the highest percentage of the igneous rock fragments would imply the sands were a product of mixing quartz-rich sands with little or no mafic minerals with sands rich in igneous rock fragments. Niggli mg⁺ is used primarily to deduce igneous fractionation in basic and ultrabasic rocks where Mg decreases with increasing total iron. A plot of mg⁺ verses si⁺ (Fig. 5.3.10) does not reveal a similar negative trend observed in the fm⁺-si⁺ plot for the Straiton sandstones. The negative correlation in Fig. 5.3.9 is more accurately explained by the loss of unstable mafic minerals during sedimentary transport accompanied by enrichment in stable minerals, mainly quartz, and is not a product of igneous fractionation. The absence of any sedimentary fractionation in the H-T-C-NE sandstones suggest that mixing took place after deposition of the sands in the sedimentary basin reflecting the overall immaturity of these sands.

The high temperature chemistry of divalent magnesium and iron is clearly linked, both have similar ionic radius and chemical attributes. Mutual substitution is widespread in a variety of minerals. It is therefore not surprising that strong correlations exist between MgO-FeO. The trivalent chromium ion has chemical properties similar to Al³⁺ and Fe³⁺. Ni²⁺ has a similar ionic radius to Mg²⁺ to which it commonly shows a positive correlation. Ni and Cr are usually associated with early crystallization in magmatic rocks in the form of chromite, a spinel where Cr³⁺ substitutes for Al³⁺, and olivine where Ni²⁺ substitutes for Mg²⁺. The preference of Cr and Ni for early crystallates and relative immobility of these elements make these elements excellent indicators of basic and ultrabasic source rocks.

In contrast to Cr which lacks a positive correlation to fm⁺ (Fig. 5.3.11 a-b) Ni shows a positive correlation to fm⁺ (Fig. 5.3.12 a-b) although there is considerable scatter in both areas. It is feasible to assume Cr is mainly associated with refractory minerals which may have had more than one cycle of sedimentation and not concentrated in the basic igneous

fragments. Negative trends between Si^{+4} and Mg^{+2} along with positive trends between Cr^{+3} and Mg^{+2} (Fig. 5.3.13 a-b) and Ni^{+2} and Mg^{+2} (Fig. 5.3.14 a-b), reflecting igneous fractionation from differentiated magmas mimicked in mafic-rich sands, are not apparent in the sandstones.

A poor positive correlation between $FeO-Fe_2O_3$ in the Straiton sandstones is not present in the H-T-C-NE sandstones (Fig. 5.3.15 a-b) where there is a wide variation in Fe_2O_3 at constant FeO . The Fe_2O_3/FeO ratio for the sandstones is 0.94 and 0.88, respectively. Pettijohn (1975, table 7-3) reports ratio values of 0.46 for average greywackes and 2.71 for average lithic arenites. Rapid sedimentation of ferrous-rich turbidites accounts for the low ferric iron recorded in greywackes while loss of unstable mafic rock fragments in aerobic conditions accounts for the high ferric iron recorded in lithic arenites.

The Greywacke Conglomerate sandstone clast ratios compare more closely to the average greywackes than to lithic arenites but have higher values of ferric iron. The 'excess' ferric iron is most likely in the form of hematite which is the stable Fe^{+3} bearing mineral under oxidizing conditions. The increase in Fe_2O_3 can have several origins.

- 1). The diagenetic alteration of original Fe^{+2} rich oxides and silicates where Fe^{+2} is released outward from decomposing grains and redistributed by oxygenated pore fluids. A negative correlation between FeO and Fe_2O_3 would be expected.

- 2). Introduction of detrital Fe^{+3} -rich minerals such as hematite and/or magnetite, ferric iron absorbed on clays or colloidal ferric iron in circulating ground water.

Many of the clasts show deep penetration of reddening, a number of clasts when cut in half are half red and half green. The irregular nature of the red pigment and the lack of correlation between Fe_2O_3 with refractory minerals such as Zr and P_2O_5 , (Tables 5.3.1-5.3.2), implies the introduction of significant amounts of detrital Fe^{+3} oxides was not the sole agent responsible for the excess ferric iron. It seems logical that much of the reddening was produced during very late diagenetic alteration of source derived ferrous iron and introduction of colloidal ferric iron from fluid migration through the conglomerate giving a random variation in Fe_2O_3 at constant FeO . Faulting and fracturing may have played an important role in the migration of late fluids through the conglomerate. The positive correlation in the Straiton samples suggests alteration in the sandstone clasts was not as pervasive and much of the ferric iron was already in the oxidized state during deposition of the original sands.

A negative correlation between fm^{+2} and $al^{+2}-alk^{+2}$ in the Straiton sandstones (Fig. 5.3.16 a) implies that $MgO-FeO-Fe_2O_3-MnO$ are not associated with sheet silicates where muscovite is the dominant mineral and mainly occurs in oxides. The absence of a negative correlation between fm^{+2} and $al^{+2}-alk^{+2}$ in the Hagshaw Hills (Fig. 5.3.16 b) where muscovite is

in a higher proportion to the T-C-NE sandstones indicates that compared to the Straiton area a higher percentage of ferromagnesium elements may be associated with the alteration of original detrital basic fragments to chlorites. In the North Esk sandstones a poor positive correlation not present in the H-T-C sandstones (Fig. 5.3.16 b) occurs and suggests that the ferromagnesium elements in the North Esk area are concentrating in chlorites in preference to oxides.

Rutile is a common constituent in the sandstones and the presence of ilmenite in the H-T-C-NE sandstones is expected from the strong correlation of FeO and TiO₂ and low correlation between Fe₂O₃ and TiO₂, since ilmenite has only limited substitution of ferric iron into the crystal structure (Deer *et al.*, 1978). A positive correlation between ti^{\wedge} and $al^{\wedge}-alk^{\wedge}$ in the Straiton sandstones, (Fig. 5.3.17 a), confirms that much of the Ti is incorporated into the sheet silicate structure and associated with metamorphics. In contrast, there is an absence of correlation between the ti^{\wedge} and $al^{\wedge}-alk^{\wedge}$ in the H-T-C-NE (Fig. 5.3.17 b), Ti probably widely distributed between both oxides, chlorites and possibly muscovites. The increase in ti^{\wedge} with chemical maturity (si^{\wedge}) in the Straiton sandstones, (Fig. 5.3.18), does not occur in the H-T-C-NE where ti is also associated with detrital basic rich fragments.

The chemical properties of Co⁺² resembles ni and both usually occur together. Its ionic radius is intermediate between Mg⁺² and Fe⁺² and commonly substitutes for these two elements in silicates. In the Straiton sandstones co has a strong correlation to ni and moderate correlations to MgO, Fe₂O₃, FeO, and Al₂O₃. The high correlation to H₂O in these sandstones suggest that much of the Co is retained in the chlorite structure which can have up to 14% water in the ideal formula Mg₁₂(Si₈O₂₀)(OH)₁₆. There is a poor negative correlation between $al^{\wedge}-alk^{\wedge}$ and Co (Fig. 5.3.19 a) in the Straiton area where muscovite is the dominant sheet silicate, however, there is considerable scatter suggesting that minor substitution of co into the sheet silicates may occur. Significant trends are not apparent in the H-T-C-NE sandstones, (Fig. 5.3.19 b).

Zinc has an identical ionic radius to Fe⁺² and only slightly larger than Mg⁺², as a result Zn⁺² is associated with the bivalent cations; Ni⁺², Co⁺², Mg⁺², and Fe⁺². In the H-T-C-NE there is a strong correlation between Zn and MgO and moderate correlations with FeO, Ni, Cr, Co. In contrast, in the Straiton sandstones Zn shows only moderate correlations to cr and ni. A plot of Zn verses $al^{\wedge}-alk^{\wedge}$ (Fig. 5.3.20) shows a negative trend for the Straiton sandstones and to a lesser extent for the Hagshaw Hills and the absence of trends for the T-C-NE samples. The conclusion is zinc is mainly entering the oxides (*e.g.* spinel, magnetite, ilmenite) in the S-H but may also be located in the chlorites in the both the T-C and NE areas.

Y-La-Ce

The ionic radius and trivalent state of Y fits into the 'Lanthanide' series, La-Lu. It is convenient to separate the rare-earth elements into the light-rare-earth elements (La-Sm) and heavy rare-earth elements (Gd-Lu). Y^{+3} has a similar ionic radius to Ho^{+3} , a heavy ree, and is sometimes used as an approximation of the heavy-rare earth elements. In most common minerals, substitution for large cations such as Ca^{+2} , Sr^{+2} , and Pb^{+4} occurs. Owing to the chemical similarity of the lanthanides, all have unfilled 4f subshells which are shielded by eight electrons and thus are not involved in significant chemical interactions, an association of the lanthanides in the host minerals is common.

Y is most strongly correlated with TiO_2 , P_2O_5 , Zr, Ce, La in the all the sandstones and Al_2O_3 in the H-T-C-NE. A plot of $al^{+4}-alk^{+4}$ versus Y (Fig. 5.3.21 a-b) shows no significant trends in the sandstones and is probably widely distributed among the refractory minerals, substituting for Ti^{+4} in rutile and ilmenite, Ca^{+2} in apatite and sphene, Zr^{+4} in zircon, as well as substitution of Y for Ti in the sheet silicates. The correlation of Y with Al_2O_3 and to a smaller degree Fe_2O_3 , FeO, MgO and H_2O in the H-T-C-NE indicates that Y has been fixed in the chlorites associated with the breakdown of original detrital ferromagnesium minerals. La and Ce show a high degree of mutual correlation and are most strongly associated with Zr.

Negative or positive trends between $al^{+4}-alk^{+4}$ vs La (Fig. 5.3.22 a-b) and Ce (Fig. 5.3.23 a-b) are not apparent.

U-Th-Pb-Cu

Divalent Pb is more common than tetravalent Pb in the earths crust (Wedepohl, 1974) and substitutes for large mono- and divalent cations K^{+} , Sr^{+2} , Ba^{+2} as well as the smaller ions Ca^{+2} and Na^{+} . The substitution of Pb for large cations leads to higher Pb concentrations in potassium feldspar and micas. In the Straiton sandstones Pb correlates most closely with K_2O but does not show a preference for the muscovites (Fig. 5.3.24 a), indicating a dual location for both K-feldspars and muscovite. In the H-T-C-NE samples Pb has a preference for MgO but is it unclear where the majority of Pb is located, however, is not preferentially taken into the sheet silicate structure, (Fig. 5.3.24 b).

Th and U belong to the Actinium series which is analagous to the Lathanide series but have incomplete 5f shells. Th has the highest correlations with K_2O , Rb, Ba in the H-T-C-NE but is also correlated with Zr and TiO_2 in the Straiton sandstones. Fig. (5.3.25 a-b) shows that Th is not concentrated in either the feldspar or micas, having a dual location in both minerals. Uraniums low concentration and subsequent low variations most likely account for

the low correlations of U within both groups of sandstones.

Cu occurs in nature in three valence states (Cu , Cu^+ , Cu^{+2}), Cu^+ and Cu^{+2} being the most common in the rock forming minerals. Cu^+ has a similar ionic radius to Na^+ and Cu^{+2} has a similar ionic radius to Fe^{+2} . However, strong correlations to either element are not apparent.

Zr-Ga-Nb-MnO

Zircon is the most important mineral of zirconium. Zr is typically low in plagioclase, olivines and orthopyroxenes but can occur in significant amounts in micas, clinopyroxenes, amphiboles and garnets. Zr^{+4} can substitute for Ti^{+4} and a high correlation between TiO_2 and Zr in the sandstones indicates that Zr is partitioned between both zircon and Ti-bearing minerals, mica, rutile, and sphene.

Mn^{+2} is the common valence state for manganese in rock forming minerals and can substitute for ions of similar size elements such as Mg^{+2} , Fe^{+2} , Ca^{+2} , as well as Fe^{+3} and Al^{+3} . Ferromagnesian minerals commonly contain higher concentrations of MnO than feldspars and micas. In the Straiton sandstones MnO shows a moderate correlation to MgO and H_2O indicating incorporation of MnO into the chlorite structure. In the H-T-C-NE samples MnO has an absence of any strong correlations.

The distribution of Ga is dominantly controlled by Al^{+3} with which it is chemically similar and frequently associated. Ga^{+3} has the same ionic radius as Fe^{+3} but is chemically more closely related to Al^{+3} . The association between Al and Ga is reflected in the high correlation between Al_2O_3 and Ga in both the groups of sandstones, Ga being widely distributed in all the al-bearing minerals.

A close association exists between Nb^{+5} and Ti^{+4} and substitutions of Nb for Ti in minerals such as ilmenite, rutile, sphene, and micas are common. Positive trends between Nb and Al^{+3} are absent (Fig. 5.3.26 a-b) indicating the dual location of Nb between the refractory minerals and sheet silicates in these sandstones.

5.4. Tectonic implications of the geochemical data and comparison to the Southern Uplands greywackes and Midland Valley lithic arenites in the Crawton Basin.

The previous sections defined two chemically distinct suites of sandstones, the Straiton and H-T-C-NE areas. Chemical variation between the two suites of sediments has been shown to be the result of compositional variation, which is mainly controlled by the geotectonic setting during deposition of the sandstones. The chemical composition of sandstones and its relation

to tectonic setting has been studied by a number of authors (Crook, 1974; Schwab, 1975; Maynard *et al.* 1982; Bhatia, 1983, Bhatia and Crook, 1986). Clear chemical distinction is usually apparent between quartz-poor (58%-62%, SiO₂) intra-oceanic fore-arc sediments and quartz-rich (avg. > 77%, SiO₂) passive margin, trailing-edge, sediments. However, subdivisions of active tectonic settings; strike-slip orogens, active continental margins, and both continental and intra-oceanic back-arc basins, usually associated with intermediate-quartz (68%-74%, SiO₂) sandstones show considerable overlap in both major and trace-element geochemistry.

One of the most distinctive major element parameters used for discrimination of tectonic setting is the ratio K₂O/Na₂O. The K₂O/Na₂O ratio for trailing-edge modern sands and sandstones is typically greater than 1.0 and compares with a mean K₂O/Na₂O (1.40) in the Straiton sandstones. The K₂O/Na₂O ratio for the H-T-C-NE areas are closely related giving mean values of (0.76, 0.61, 0.60, 0.61), respectively. Values in this range are typical of active tectonic settings and include back-arc basins (0.56), strike-slip margins (0.74) and, continental island-arcs (0.72), (Maynard *et al.* 1982). High SiO₂ and K₂O/Na₂O ratios suggest a passive-margin setting for the Straiton sandstones and compare with modern passive-margin sediments (Fig. 5.4.1), although variation is high in the Straiton samples many plotting outside the graph area at high SiO₂/Al₂O₃. The H-T-C-NE sandstones fall outside both the passive margin settings and active tectonic fields having K₂O/Na₂O ratios typical of 'active tectonic settings' but high SiO₂/Al₂O₃ ratios typical of passive margin settings. High silica values are a feature of the sediments, where high-grade metamorphic silicic fragments are frequent in the H and acid volcanic fragments in the NE (see sect 4.3.1). The T-C samples are the least siliceous but still contain significant amounts of both acidic volcanics and metaquartzites. The high silica index thus displaces the H-T-C-NE sandstones toward higher SiO₂/Al₂O₃ ratios than would be expected in active tectonic settings.

Total Fe₂O₃ and MgO is also widely used to discriminate sandstones from various tectonic settings. Modern sands from passive margins have average total Fe₂O₃ + MgO values less than 5.0 (volatile-free) and compare with a mean of 5.04 in the Straiton sandstones, the clasts from the easterly exposures, section 1, having lower mean values (3.42) than the westerly exposures (6.64), section 2. The H-T-C-NE have significantly higher mean total Fe₂O₃ + MgO values of 7.01, 8.05, 7.68, 7.79, respectively, and compare with modern sands from back-arc basins, continental island arcs, and strike-slip active margins. However, a small proportion of ferric iron may have been introduced in these sandstones which would lead to higher total Fe₂O₃ + MgO values. Modern sands from intra-oceanic fore-arc basins have total Fe₂O₃ + MgO values typically in excess of 8.0. The two parameters, K₂O/Na₂O and total Fe₂O₃ + MgO, can be used to effectively discriminate between passive margins and

oceanic-arc settings but however considerable overlap can exist in the subdivisions of active tectonic settings. The discrimination based on these two parameters for the Greywacke Conglomerate sandstones places the Straiton sandstones into a category closely resembling the passive margin modern sands, particularly samples from section 1, and the H-T-C-NE sandstones into the modern sands derived from active margin settings. Chemical signatures typical of modern oceanic fore-arc sands, high total $\text{Fe}_2\text{O}_3 + \text{MgO}$ along with low SiO_2 and K_2O are not observed in the Greywacke Conglomerate.

Bhatia (1983) studied a suite of Palaeozoic turbidites in eastern Australia ranging from silica-poor to silica-rich and found that various major element parameters plotted against total $\text{Fe}_2\text{O}_3 + \text{MgO}$ can be used to effectively discriminate the tectonic settings in these ancient sandstones. Fig. (5.4.2 a-d) shows the major oxide geochemical parameters used to differentiate the tectonic fields in eastern Australia relative to the location of the sandstones in the present investigation. The majority of the samples plot outwith the defined tectonic settings reflecting the individual nature of the two suites of sandstones. However, several conclusions can be drawn from the comparisons. Although there is significant scatter in the total $\text{Fe}_2\text{O}_3 + \text{MgO}$ in the Straiton sandstones ranging from passive margin settings to island-arc settings, the majority have values typical of passive and active continental margins. In contrast, the majority of the H-T-C-NE sandstones overlap with values typical of continental-island arcs and oceanic-island arcs. The variation in the Straiton area is controlled in part by the lower total $\text{Fe}_2\text{O}_3 + \text{MgO}$ in the easterly exposures compared to the westerly exposures but also by the variation of this parameter within the westerly exposures and associated inhomogeneity of this section (see sect. 5.5.2).

Fig. (5.4.2 a) shows the H-T-C-NE cluster in the continental island-arc with some overlap into the island-arc field but have higher $\text{K}_2\text{O}/\text{Na}_2\text{O}$ values than would be expected in island-arc sandstones. Many of the samples in both the Straiton and H-T-C-NE areas fall well outside the plot at extremely high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios, particularly the Straiton samples with < 5.0 total $\text{Fe}_2\text{O}_3 + \text{MgO}$ (section 1). The high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios reflect the abundance of detrital muscovite and would discriminate against an oceanic-island arc setting and favour the continental-island arc for the H-T-C-NE sandstones. The exceptionally low Na_2O values recorded in the Straiton section 1 samples and subsequent high SiO_2 & low total $\text{Fe}_2\text{O}_3 + \text{MgO}$ indicate that the original quartz-rich sand which gave rise to the abundant metaquartzite was originally clean passive-margin quartz with little or no mixing with 'active' margin sands. Similarly, subsequent uplift of the metamorphic products and deposition with limited, if any, introduction of basic fragments suggest the final depositional basin was again a passive margin setting.

The contribution from TiO_2 -rich muscovites displaces the sandstones to higher values of TiO_2 relative to the tectonic fields, (Fig. 5.4.2 b). The majority of the Straiton samples have higher values of TiO_2 relative to the passive and active margin settings whereas many of the H-T-C-NE samples, which also have significant amounts of TiO_2 -rich muscovites (see sect 5.3), are shifted into the oceanic-island arc field. Low CaO values in both the carbonate-poor and carbonate-removed Midland valley samples give rise to high $\text{Al}_2\text{O}_3/\text{CaO} + \text{Na}_2\text{O}$ ratios which also plot outwith the tectonic fields, (Fig. 5.4.2 c). Significant scatter seen in the Straiton sandstones is mainly controlled by the variation in Na_2O values between section 1 and section 2 samples along with inhomogeneity within the section 2 samples. Fig. (5.4.2 d) shows the least amount of variation with many of the Straiton sandstones associated with passive margin and active margin settings. The H-T-C-NE sandstones cluster below the continental island-arc field having high SiO_2 values.

In general, the Straiton and H-T-C-NE sandstones do not compare with the tectonic fields defined for the eastern Australian sediments but when the effects of a significant amount of ti-rich muscovites and metaquartzites are removed two patterns emerge; 1). the Straiton sandstones are predominantly associated with the non-subduction passive margins (especially the easterly exposures, section 1) and active margins, a contribution from arc-derived material may have been added at various times to the westerly exposures, section 2 and, 2). the H-T-C-NE sandstones are associated primarily with the continental island-arc field. A pre-existing orogenic metamorphic belt contributed a significant amount of metamorphic detritus to the Midland Valley clasts offsetting the major-element geochemistry towards high SiO_2 , TiO_2 , and K_2O .

Bhatia and Crook (1986) also proposed a correlation between trace-element geochemistry and tectonic setting. The ratio of La to Th was found to discriminate between oceanic and continental island-arcs. Fig. (5.4.3 a) shows very little variation in the Th content between the sandstones (avg. 6-8), values typical of continental island-arcs and low for quartz-rich sandstones where Th values are typically greater than 12 (Taylor and McLennan, 1985). Thorium has been shown to be immobile and enriched in deeply weathered soils (Kronberg *et al.* 1979) and would suggest that the source terrain for all the sandstones including the Straiton sandstones was low in Th abundances compared to average upper crustal values (10.7 ppm) recorded by Taylor and McClennan (1985). Low Th values may suggest that granitic detritus is low in these sandstones. La is not positively correlated to Th in the present samples under investigation which is in contrast to the Australian samples, $r=0.79$ (Bhatia and Crook, 1986), a correlation also noted by McClennan (1980). The sandstone samples from the Straiton and H-T-C-NE areas show considerable variation in La at constant Th. La is associated with refractory minerals whereas Th is associated K-bearing feldspar and micas

(see sect. 5.3). The lack of correlation may reflect the different behaviour between La and Th during sedimentary processes but also may reflect the introduction of these two elements from two distinct source terrains.

A more informative plot is the $\text{Th-Co-Zr}/10$, (Fig. 5.4.3 b), which shows a clear clustering of Straiton sandstones into the passive margin field and H-T-C-NE samples into the continental island-arc field with some overlap into the island-arc field.

The La/Y, the light to heavy rare-earth, ratio given by Bhatia and Crook (1986) has been shown to increase from oceanic island-arc (< 0.5), continental island-arc ($0.5-1.0$), to active continental margins and passive margins ($1.0-1.5$). The Greywacke Conglomerate samples show no systematic variation with average ratios for the Straiton (0.76), Hagshaw Hills (0.83), Tinto (0.57), Carmichael (0.83), and North Esk (0.64) samples typical of continental island-arc margins. Again, variation between the Straiton sandstones is high with samples from section 1 having a higher ratio (avg. 0.84) than samples from section 1 (avg. 0.68). Although, the ratios are low compared to the tectonic settings suggested by the major element chemistry the ratios indicate a higher mafic input for the Tinto and North Esk samples.

Haughton (1988) described first cycle lithic arenite clasts from conglomerates in the Lower Old Red Sandstone Crawton Group, northeastern Midland Valley. The lithic arenite clasts were shown to be derived from a source within the Midland Valley and are both geochemically and isotopically distinct from the Southern Uplands greywacke sediments.

A series of bivariate and triangular plots, (Fig. 5.4.4 a-g), were used for comparison between the lithic arenites, Southern Upland greywackes, and 60 randomly selected fine to coarse-grained sandstone clasts from the Greywacke Conglomerate. In Fig. (5.4.4 a) four distinct fields can be delineated from the major element chemistry with a progressive shift towards higher silica and alkalis from the Ordovician sediments to the Straiton sandstone clasts. These four distinct fields are reproduced in Figs. (5.4.4 b-e) where the Southern Uplands sediments are characterized by high aluminum, total iron, magnesium, Cr and Ni and low silica. In all cases, the Crawton Group lithic arenites cluster with the H-T-C-NE samples with which geochemically they are indistinguishable but distinct from the Straiton samples. There is very limited overlap in the major element geochemistry with only the most siliceous Silurian sediments showing a similar chemistry to the more mafic H-T-C-NE samples.

The trace element chemistry is not as useful as the major element geochemistry in defining clear trends between the Midland Valley sandstone clasts and the Southern Uplands

sediments. Fig. (5.4.5 a) shows that while there is a separate field for low Zr-high TiO_2 Ordovician sediments, the Silurian sediments have Zr and TiO_2 values similar to the Midland Valley sandstone clasts. However, the Silurian sediments are characterized by higher Rb (Fig. 5.4.5 b) and may reflect the higher proportion of acidic volcanic fragments associated with the Silurian sediments (see sect 4.3.2). The Ordovician and Silurian Southern Uplands sediments have, in general, higher sr contents than either the lithic arenites or the Greywacke Conglomerate sandstone clasts.

Haughton (1988) has used high Cr values (up to 700 ppm), particularly in reference to metagreywacke clasts associated with and chemically similar to the lithic arenites in the Crawton Group, as an indicator of a possible ophiolitic source. Anomalously high Cr concentrations are rare in the Greywacke Conglomerate clasts but do occur particularly in the North Esk samples where 7 out of 64 samples recorded values > 300 ppm (max 679 ppm) and Carmichael samples where 2 out of 7 samples gave high Cr values > 300 ppm (max 616 ppm). These are in contrast to the Hagshaw Hills (0 out of 44), Tinto (0 out of 16) and Straiton samples (1 out of 73, max 372 ppm Cr). Average Cr values for the Straiton, Hagshaw Hills, Tinto, Carmichael and North Esk areas are 72 ppm, 110 ppm, 133 ppm, 267 ppm, and 155 ppm, respectively. All the areas have Cr values which are not inconsistent with material derived from calc-alkali basalts and high K-basalts from continental margins island arcs (avg. 235 ppm Cr). Typical oceanic island-arc basalts and ocean floor basalts have only slightly higher average Cr at 250 and 300 ppm Cr, respectively, (Shiraki, 1978). It is therefore not necessary to invoke an ophiolitic source to account for Cr values of 300-700 ppm, the range associated with the Ordovician Southern Upland sediments rich in andesitic detritus. The Silurian Southern Uplands sediments have typical Cr values intermediate between the Greywacke Conglomerate-Crawton Group clasts and the Ordovician sediments, where there is little mafic but abundant acidic volcanic debris.

The major and trace element data define four distinct groups of sediments; the Straiton, the H-T-C-NE including the lithic arenites of the Crawton Group, the Southern Upland Ordovician, and the Southern Upland Silurian sediments. The implication is that neither the Straiton or the H-T-C-NE sandstone clasts could have been derived from the Southern Uplands. The isotopic difference between the Crawton Group lithic arenites and the Southern Uplands sediments (Haughton, 1988) along with the chemical similarity to the H-T-C-NE group supports the conclusion that the Greywacke Conglomerate clasts are derived from a source other than the Southern Uplands greywackes. The Straiton sandstones are chemically distinct from both the Southern Uplands sediments and the Crawton Group clasts.

5.5 Principal Component Analysis (Vertical and lateral trends).

Principal Component Analysis was used to delineate vertical and lateral geochemical trends within the individual Greywacke Conglomerate sections and between the major Greywacke Conglomerate outcrops studied. Although broad lateral geochemical trends have been identified in sections (5.1-5.4), principal component analysis uses a quantitative statistical method to describe the variation-covariation between the major and trace element data.

Principal Component Analysis (R-mode Factor Analysis) is analogous to Q-mode Factor Analysis (see sect 4. 4) but instead of determining the inter-correlations between the samples the method is used to resolve the relationship between a set of variables (the major and trace element data). The mathematical procedure used in P.C.A. is very similar to Q-mode Factor Analysis and only the major differences between the two methods will be outlined. Additional mathematical procedures and applications of P.C.A. to geochemical data can be found in; Joreskog *et al.* (1976), Davis (1986), Bhatia (1986), Spencer (1966), and Cameron (1968).

The data matrix consists of all the Greywacke Conglomerate samples, 203 rows, and 29 variables or columns. The variables used were the Niggli numbers, the trace element data transformed to log to the base 10, the grainsize (gran-v.c.=2, v.c.-c.=1, c.-m.=0.5, m.-f.=0.25, f.-v.f.= 0.125) and the mineralogical maturity index given by the ratio of total Qm+Qp to Qm+Qp+feldspar+rock fragments. The data matrix was scaled leaving the range of the values to lie between 0 and 1 in order to eliminate any possible effect between different units of measure and insure that variables with a small range will have the same influence as variables with a large range. A correlation matrix was computed and a new set of variables, factors, and associated eigenvalues were determined, similar to the method described in (sect 4.4). The eigenvalues are low in all the factors and underline the widespread nature of the chemical elements in a number of host minerals as well as the overall geochemical similarity of the samples. A schematic diagram showing the first 7 factors which account for 71% of the total variation is shown in Fig. (5.5.1).

The first factor can be termed the mineralogical maturity factor and accounts for the highest percentage of variation, 28%, within the data. The highest loadings on the positive end can all be accounted for by quartz and muscovite which increase with increasing mineralogical maturity. The highest negative loadings on factor I are all associated with the ferromagnesium elements, the only surprise being Sr which has been shown to correlate with albite (at least in the H-T-C-NE) and supports the argument that Sr was originally associated with ca-plagioclase, a mineral expected to increase with increasing ferromagnesian. TiO_2 is more closely associated in the sediments with the micas than the ferromagnesian minerals.

The second factor can be termed the textural maturity factor. The positive end represents the proportion of rock fragments where magnesium, silica, and iron increase with increasing volcanic fragments and metamorphic quartz-rich fragments. The highest loadings on the negative end are all immobile elements which concentrate in texturally more mature sediments.

The presence of K^+ in both the positive end (k^+) and the negative end (alk^+) in factor III would indicate that the negative loading was dominantly controlled by Na_2O . The negative loading would thus be associated with sodic plagioclase and the positive loading with both muscovite and orthoclase but predominately muscovite since Rb as opposed to Ba is represented.

Factor IV shows that La, Ce, and Y is associated with ferromagnesian minerals (heavy minerals, oxides, mafic rock fragments) as well as plagioclase feldspar in Factor III but does not enter the orthoclase or muscovite structures which Ba and Rb are strongly associated.

The positive loadings on Factor V equate mainly with the sheet silicates where w^+ (H_2O) as OH^- is an integral part of the structure, particularly in the chlorites. Cu has a high positive loading indicating incorporation into the sheet silicate structure where previously no clear correlation with any mineral was found. The negative loading shows the correlation between Th, U and fm^+ and indicates a decrease in these elements with increasing formation of chlorite. Previously, it was recognized that Th showed the strongest correlation to K_2O , Rb and Ba in the H-T-C-NE (sect 5.3.1) and the correlation with fm^+ may be more strongly controlled by U.

Factor VI shows Zr and ti^+ , associated with heavy minerals, correlates with Cr indicating that Cr-rich oxides possibly magnetite, ilmenite, or chromite may be the main host for Cr. The negative loading of Sr, k^+ , and residual calcium (c^+) is mainly controlled by Sr substitution in K-feldspar and Ca-bearing minerals such as apatite and epidote.

Factor VII shows that mineralogical maturity can be equated with Zr and is antithetic to mg^+ and U which both increase with increasing grain size. The implication that mineralogical maturity can be solely expressed as Zr along with the association of Cr with Zr in Factor VI indicates Cr is a refractory element in these sediments which increases with increasing maturity. A conclusion already reached in section 5.3.1.

5.5.1 Lateral trends across the Greywacke Conglomerate.

In the following section each original sample has been converted to principal component scores. The factor scores (F) are simply the projection of the nth sample onto the principal axes defined by the eigenvector.

$$F=(X U_k \Gamma_k)^{-1/2}$$

X= original data matrix

U_k = first k eigenvectors

Γ_k = inverse sq.rt. of the
first k eigenvalues

The factor scores are a new set of uncorrelated variables which represent the influence of the factors on the samples, for example a high positive score coefficient in the first column would imply the original sample was strongly influenced by the high loadings in Factor I.

The mean factor scores from each major outcrop area have been plotted for each principal component axis in Fig. (5.5.2. a-g). The plots can be used to show lateral trends across the Greywacke Conglomerate from the southwest (Straiton) to the northeast (North Esk).

The mineralogical maturity (quartz and muscovite) decreases from the the Straiton area to the Tinto (mean -2.67) and Carmichael (mean -2.15) but increases in the North Esk area, characterized by abundant feldspar and rhyolitic fragments particularly in the coarser-grained samples (Fig. 5.5.2 a).

The Carmichael and Tinto samples also have the highest degree of textural maturity (Fig. 5.5.2 b) with high concentrations of immobile elements which increase with weathering and transportation of the sediments. The fact that these sediments are at present the most texturally mature suggests the proximal equivalent sediments of the Tinto-Carmichael samples were richer in mafic material. The North Esk samples show the lowest degree of textural maturity indicating the source area was not far from the deposition of the sediments. The Straiton sandstones fall just in the positive side of the principal axis. However, the samples from section 1 have a higher negative loading (-0.26) and the samples from section 2 have a higher positive loading (0.31) than the total mean. The samples from section 1, the easterly exposures, have a higher degree of sedimentary fractionation than the samples from section 2.

The negative side of Factors III equates with the presence of plagioclase feldspar and the positive side orthoclase feldspar and muscovite. The Hagshaw Hills sandstones have the highest na-plagioclase content, (Fig. 5.5.2 c), compared to the remaining areas which have muscovite and orthoclase dominant over plagioclase. Interestingly, the North Esk has as high a positive loading as Straiton indicating the increase in the proportion of orthoclase feldspar associated with acidic volcanic fragments. Although, it is not known how much influence muscovite has on increasing the positive loading in these sandstones. The Tinto-Carmichael samples are intermediate between the Hagshaw Hills and the Straiton-North Esk samples which is difficult to rationalize being the most mafic sediments. However, the presence of orthoclase has already been noted and pulls the sandstones up towards the positive end. Overall, there is very little variation across the Greywacke Conglomerate in either total alkalis or REE-rich minerals, (Fig. 5.5.2 d).

The Hagshaw Hills has a high positive loading in Fig. (5.5.2 e) not seen in the S-T-C-NE samples, reflecting higher proportions of sheet silicates and may indicate a higher degree of diagenetic alteration of original basic rock fragments and agrees with higher percentages of chlorite-altered fragments recorded in these sediments (Table 4.1). Although, chlorite is subordinant to muscovite in these sandstones (see sect. 5.3.1).

Tinto and Carmichael show the highest concentrations of Sr-bearing orthoclase and Sr-bearing Ca-minerals, particularly epidote which is abundant in these sediments, (Fig. 5.5.2 f). The North Esk has the highest positive loading on Factor IV, controlled mainly by the high concentrations of Cr. The Straiton and Hagshaw Hills show little trend toward either pole. The Hagshaw Hills shows the strongest affinity toward the negative pole (Fig. 5.5.2 g) where Zr values are highest and antithetic to magnesium minerals. Mg⁺ is highest in the Tinto-Carmichael samples with high mg⁺ on the Straiton and North Esk samples as well. However, it is not known to what extent mg-bearing carbonates has influenced the Straiton Factor VII scores.

In summary, the lateral chemical trends are similar to the petrographic results where both the mineralogical and chemical maturity decrease from the Straiton to the Tinto-Carmichael with an increase in the North Esk. The Tinto-Carmichael samples consistently show the strongest association with the principal axes where Mg has the strongest influence. The Hagshaw Hills is low in orthoclase and high in Na-plagioclase feldspar compared to the remaining areas. The Straiton and North Esk samples have the highest amount of K-bearing minerals, muscovite and orthoclase, with muscovite dominant in the Straiton and orthoclase dominant in the North Esk. The Tinto-Carmichael samples also have considerable amounts of orthoclase and poses an interesting problem since plagioclase would be expected to be

associated with high Mg and therefore higher in the Tinto-Carmichael sediments. Several possible explanations for the higher percentage of orthoclase in the T-C samples are:

- 1). A breakdown of plagioclase feldspar associated with increasing textural maturity
- 2). High amounts of detrital epidote recorded in the T-C rocks could suggest the original mafic source may have suffered considerable plagioclase epidotization
- 3). The source for the sandstones was devoid of plagioclase feldspar and rich in orthoclase feldspar, *i.e.* alkaline igneous rocks such as acidic volcanics or granites. High Mg argues against sole erosion from an acidic source and favours mixing of a basic igneous source with alkaline rocks.

5.5.2. Vertical Trends within the Greywacke Conglomerate.

The mean factor scores along the first seven principal factor axes were determined for samples collected at specific heights above the Greywacke Conglomerate and plotted in Fig. (5.5.3-5.5.6). In most cases the mean values obtained are an average from 2-6 samples, in rare instances the mean value is taken from only one sample.

The major drawback in using this method to interpret vertical trends is inherent in the nature of the sediment. Conglomerates, unlike fine-grained sediments are not homogenized through the sedimentary cycle during erosion and transportation. Instead, the proximal nature of conglomerates is associated with active tectonics which can include a number of different source materials. Using the mean of a limited number of samples upward through the vertical profile may not reflect the true average composition of the sedimentary clasts within the conglomerate at that particular horizon. A much larger number of samples would be preferred to counteract the effects of an aberrant sample associated with mixing two or more different lithological units.

In the Straiton area there is a clear separation in the chemical maturity between section 1 and section 2, (Fig. 5.5.3 a). This separation is maintained from the base to the top of the conglomerate with one exception at approximately 35 m above the base of the conglomerate. The decrease in maximum clast size from section 1 to section 2 and palaeoflow measurements (see. chap. 3) would suggest section 2 is the downfan equivalent of section 1. It can be seen that section 2 is sourced from a chemically and therefore compositionally less mature (lower factor score values) package of sediments and could not be the downfan equivalent of section 1. It is more reasonable to conclude that active faulting between the two depositional basins could have sourced two separate areas (possibly related to two different times).

Upward through the conglomerate section 1 is more uniform than section 2 which has more variation associated with repeating mature and immature sediments. Taking this

variation into consideration, section 2 shows a vertical trend toward more immature sediments where each progressive cycle upward through the section is shifted toward decreasing chemical maturity. The same is true in section 1 with decreasing maturity upward through the conglomerate.

Factor 2 (Fig. 5.5.3 b) shows that both texturally immature and mature sediments were sampled in both section 1 and section 2. A comparison between Fig (5.5.3 a and b) shows no systematic correlation between chemical and textural maturity. Therefore, the difference in chemical maturity between the sections cannot simply be explained by samples taken from sediments with distinct histories with regard to sedimentary processes, *i.e.* grain size and textural maturity

In the Hagshaw Hills area there is no distinct separation along principal axis 1 (Fig. 5.5.4 a) between sections 1 and 3 indicating the source area was the same or lithologically similar in both sections. It is therefore unnecessary to invoke deposition from more than one fan or source block. There is very little variation in the chemical maturity in either section upward through the conglomerate. Overall, the source rock supplying the Hagshaw Hills basin was a thick chemically homogeneous package of sediments. Again there is no correlation between textural and chemical maturity (Fig. 5.5.4 a-b).

In the Tinto area there is an upward change to more mature samples and back into immature sediments, (Fig. 5.5.5 a). This vertical change is mimicked in Fig. (5.5.5 b) where chemical maturity correlates with increasing textural immaturity, a function of quartz-rich rock fragments. In the Tinto region the chemical vertical variation can be explained by textural variation between the samples. However, samples from the base of the conglomerate are more texturally mature & chemically immature than the samples from the top of the conglomerate suggesting an overall trend toward chemical maturity upward through the section.

The upward vertical trend in the North Esk is toward increasing chemical maturity, (Fig. 5.5.6 a). There is no definitive correlation between textural and chemical maturity within each section however the majority of samples from section 2 are texturally more immature than section 1. The higher values along principal axes 1 seen in section 2 may in part be to variation in grain size and texture but more importantly may also reflect two distinct sources.

There is a definite upward increase in the percentage of plagioclase feldspar and concomitant decrease in muscovite (lower values) in Straiton section 2, (Fig. 5.5.3 c). Vertical trends are not clearly defined in section 1. In Fig (5.5.3 d) section 1 shows an overall increase

in alkalis where lower values are associated with increasing orthoclase and/or muscovite. Overall vertical changes in the percentage of K-feldspar and muscovite in section 1 are not apparent. Decreasing chemical maturity along with increasing plagioclase & decreasing muscovite in section 2 and increasing K-feldspar & muscovite in section 1 suggests a predominance of feldspar-rich volcanic rock fragments over low-grade metamorphic rock fragments in section 2 and low-grade metamorphic fragments with or without K-bearing volcanics over quartz-rich fragments in section 1 vertically upward through the conglomerate.

In the Hagshaw Hills area section 1 and to some extent section 3 shows an increase in the percentage of plagioclase feldspar from the base of the conglomerate through to the top of the conglomerate (Fig 5.5.4 c). Vertical changes in the percentage of K-feldspar/muscovite are not discernable (Fig. 5.5.4 d). To compensate for an increase in plagioclase-rich rock fragments while maintaining chemical homogeneity throughout the conglomerate without introducing acidic fragments, an increase in polycrystalline quartz from veins and/or metaquartzites would be expected.

A definite overall vertical change in feldspar compositions is not seen in the Tinto region (Fig. 5.5.5 c-d). In the North Esk area, section 1 shows an overall vertical trend toward increasing plagioclase feldspar (Fig 5.5.6 c) accompanied by decreasing K-feldspar (Fig. 5.5.6 d). In this section chemical maturity increased and suggests an upward increase in both basic and quartz-rich & mica-poor rock fragments with a dominance of quartz-rich over basic fragments. In contrast, there is an increase in K-feldspar upward through section 2 which may be associated with increasing plagioclase feldspar particularly in the upper half of the conglomerate. The increase in chemical maturity associated with increasing K-feldspar in this section indicates an overall increase in acidic volcanic fragments which may also be accompanied by a lower proportional increase in basic fragments. The compositional difference between the two sections indicates the variation seen in chemical maturity is controlled more by compositional than textural variation.

Factor V has been interpreted as the proportion of sheet silicates, particularly diagenetic alteration of basic igneous fragments to chlorite. In general, the sections which show an increase in basic igneous fragments upward through the conglomerate also show an increase in diagenetic alteration, (Figs. 5.5.3-6 e).

Increasing positive values along both principal axes 6 and 7 are associated with heavy minerals including Cr-bearing (axis 6) and Mg-rich minerals (axis 7). In the Straiton area section 1 does not show any significant vertical changes in heavy minerals (Fig. 5.5.3 f) but

does show an upward change to higher proportions of Mg-rich fragments (Fig. 5.5.3 g). Section 2 shows an overall upward increase in both Mg-rich minerals along with zircon, Ti and Cr-rich heavy minerals. This is consistent with the previous conclusions that both sections show a vertical decrease in chemical maturity.

In the Hagshaw Hills there is no significant vertical change in the heavy mineral compositions (Fig. 5.5.4 f). An increase in Mg-rich fragments in section 1 (Fig. 5.5.4 g) is in agreement to increasing plagioclase feldspar upward through the section. Section 3 shows an upward vertical tendency toward lower Mg-rich minerals and is difficult to rationalize since previous vertical trends between the two sections were similar. The difference may be related to the limited number of samples taken.

The Tinto samples show a systematic decrease in mg (Fig. 5.5.5 g) along with a slight decrease in zircon, Ti and Cr bearing heavy minerals (Fig. 5.5.5 f) and again suggests an upward vertical change to increasing chemical maturity.

In section 2 of the North Esk a decrease in the mg-rich fragments, (Fig. 5.5.6 g) along with increasing sr-bearing orthoclase & decreasing Zr, Ti and Cr-bearing oxides (Fig. 5.5.6 f) is consistent with increasing acidic volcanics upward through the section. Section 1 does not show the same vertical trends as section 2.

In general, the vertical trends suggest that the conglomerates become progressively more similar upward through the section to conglomerates in the adjacent eastern basin, *e.g.* the top of the Straiton conglomerates resemble the Hagshaw Hills conglomerates and the top of the Hagshaw Hills resemble the Tinto-Carmichael, *etc.*

5.6 Conclusions.

1). The Straiton samples are geochemically distinct from the H-T-C-NE samples. The H-T-C-NE have a number of significant similar chemical oxides and elements which suggest a similar source for these sandstones.

2). The chemical classification for the Straiton sandstones, arkoses and subarkoses, is misleading. It assumes that the only source of potassium is K-feldspar whereas the high potassium is the result of a high percentage of metamorphic detritus, *i.e.* low-grade, muscovite-bearing schists coupled with orthoclase-bearing metaquartzites, and not granitic detritus.

3). The sheet silicates in both the Straiton and Hagshaw Hills is predominantly muscovite whereas in the T-C and NE samples chlorite is also present. A small number of samples from the North Esk have high percentages of muscovite and are devoid of chlorite, similar to the S-H samples.

4). The Straiton sandstones are depleted in Na-plagioclase and the H-T-C-NE samples are enriched in Na-plagioclase. The Straiton, Tinto-Carmichael and North Esk samples all contain a significant proportion of orthoclase. The Tinto-Carmichael having a higher ratio of orthoclase to muscovite than the remaining areas.

5). The H-T-C-NE samples are the product of mixing mafic-rich sands with quartz-rich sands with little sedimentary fractionation. In contrast, the Straiton samples are quartz-rich sands which have lost mafic material through sedimentary fractionation.

6). Considerable amounts of Ti has been introduced from metamorphic fragments, particularly in the Straiton samples. Ti is also associated with mafic minerals in the H-T-C-NE samples. Cr is mainly located in refractory minerals which could have an ultimate source in basaltic rocks but need not be derived from an ultrabasic ophiolitic source.

7). Straiton section 1 samples geochemically resemble both modern and ancient passive margin sands. The H-T-C-NE samples resemble active tectonic settings, particularly continental island-arc settings defined for Palaeozoic Australian turbidites. Samples from Straiton section 2 show a large variation from active-continental margin to oceanic island-arc settings, although, a larger proportion cluster in the active-continental margin setting.

8). The major and trace element data define four distinct groups of sediments; the Straiton, H-T-C-NE including O.R.S. Crawton Group sandstone clasts from the northeastern Midland Valley, S.Uplands Silurian and S. Uplands Ordovician.

9). Principal Component Analysis closely compares with the petrographic results where there is a systematic decrease in geochemical maturity (quartz & metamorphics) from the Straiton to the Tinto-Carmichael with an increase in the North Esk samples. P.C.A results for the relative abundance of muscovite and feldspar agrees with previous interpretations where the areas are characterized by: Straiton- high (muscovite & orthoclase)/ Na-plagioclase, Hagshaw Hills- high Na-plagioclase/orthoclase, Tinto/Carmichael- high orthoclase/muscovite, North Esk- high (orthoclase and/or muscovite)/Na-plagioclase.

10). Straiton section 1 samples could not be the source for the samples from section 2 but may have included some reworked samples from section 1. Both the Straiton sections show a vertical decrease in chemical maturity upward through the conglomerate. No vertical trends are apparent in the Hagshaw Hills samples and a vertical increase in chemical maturity is suggested for the Tinto-Carmichael and North Esk samples.

Sources for figures in Chapter 5

Fig. 5.4.1 Tectonic settings for modern sands from Maynard *et al.* (1982)

Fig. 5.4.2 Tectonic settings for ancient sandstones from Bhatia and Crook (1986)

Fig. 5.4.3 Tectonic settings for ancient sandstones from Bhatia (1983)

Fig. 5.4.4 Data from Haughton (1988), Thirlwall (1983), and Walton (1955)

Fig. 5.4.5 Data from Haughton (1988), Thirlwall (1983), and Halliday *et al.* (1979)

Δ - Straiton
 \circ - Hagshaw Hills
 $+$ - Tinto/Carmichael
 \times - North Esk

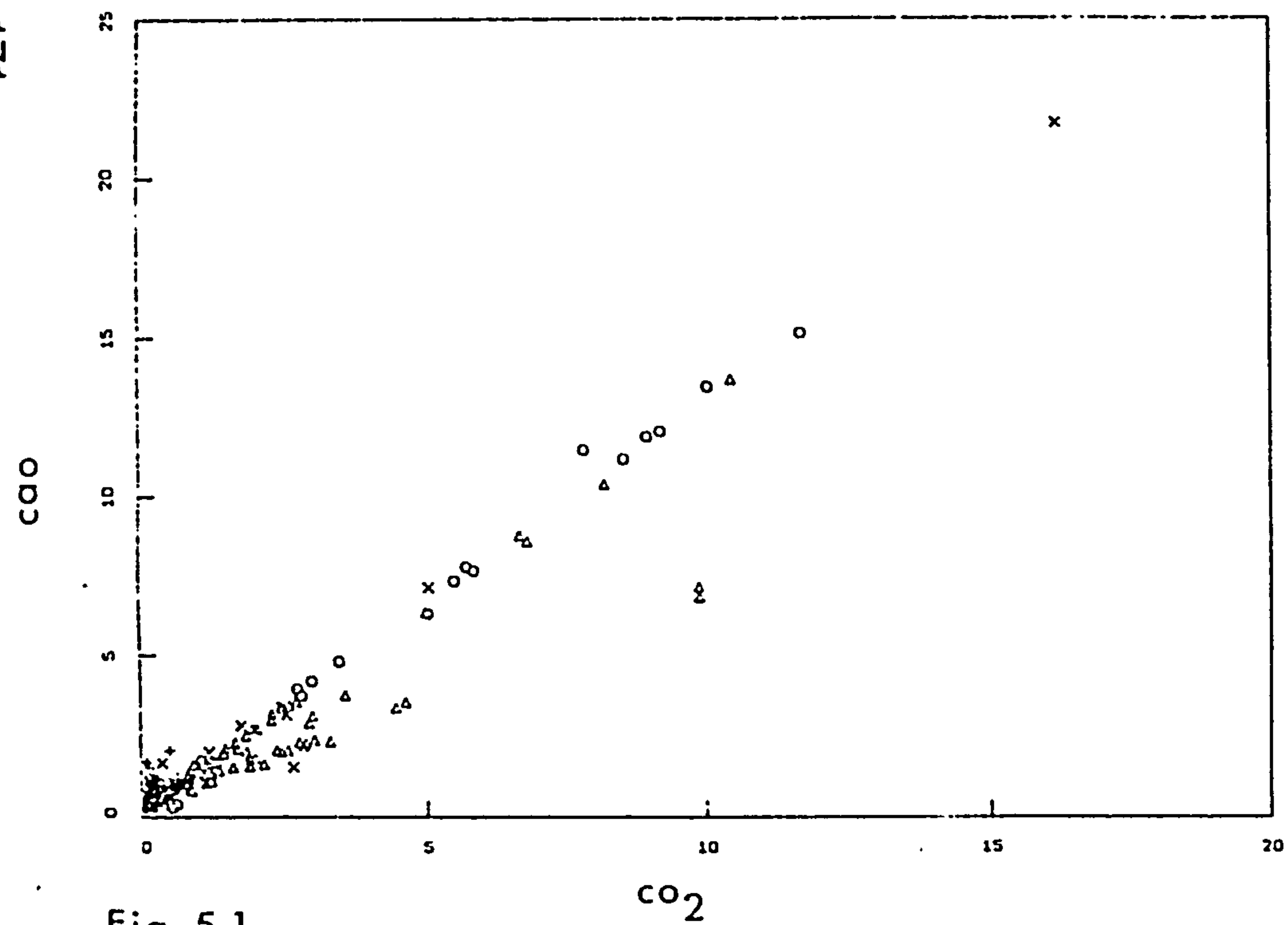


Fig. 5.1

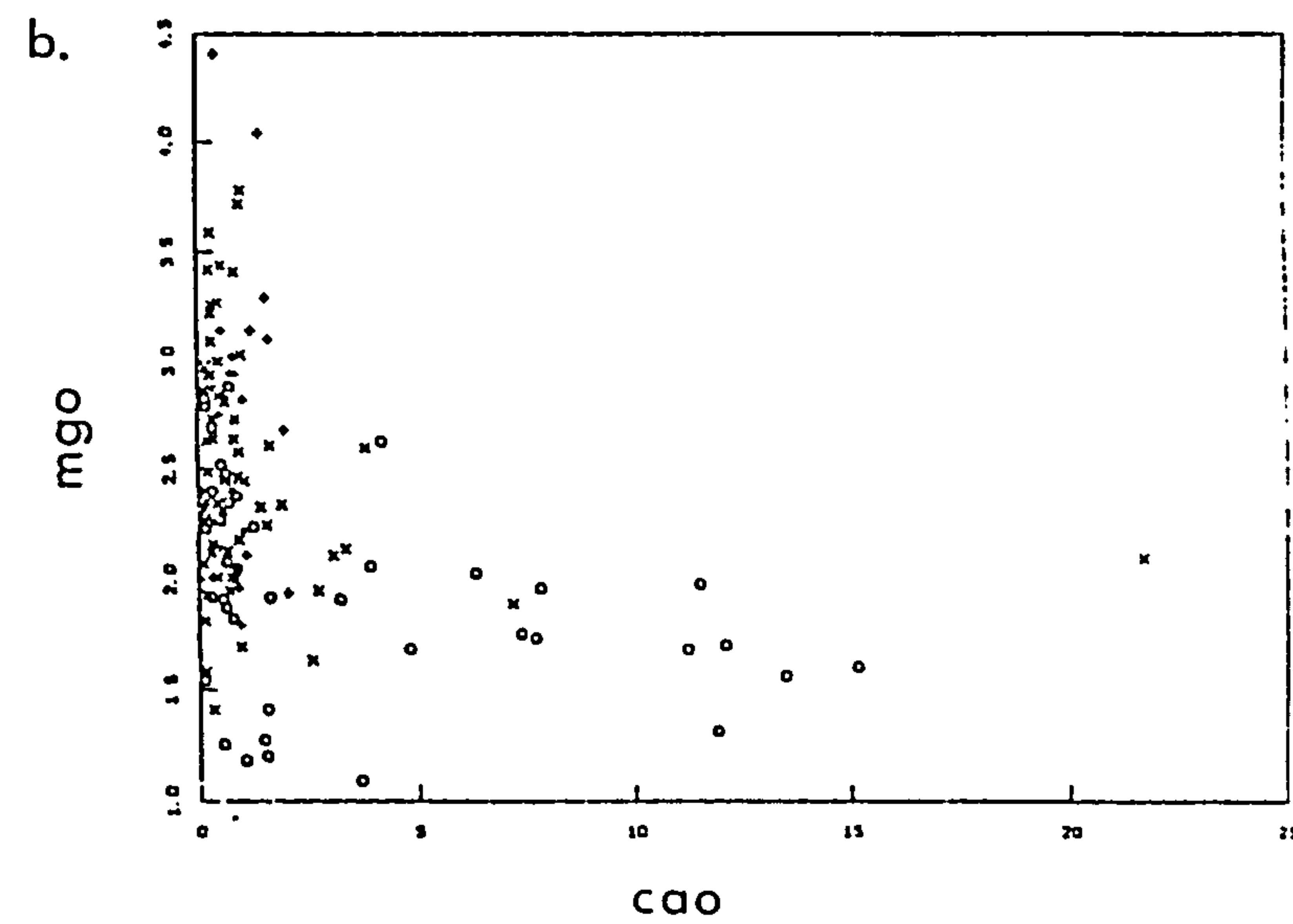
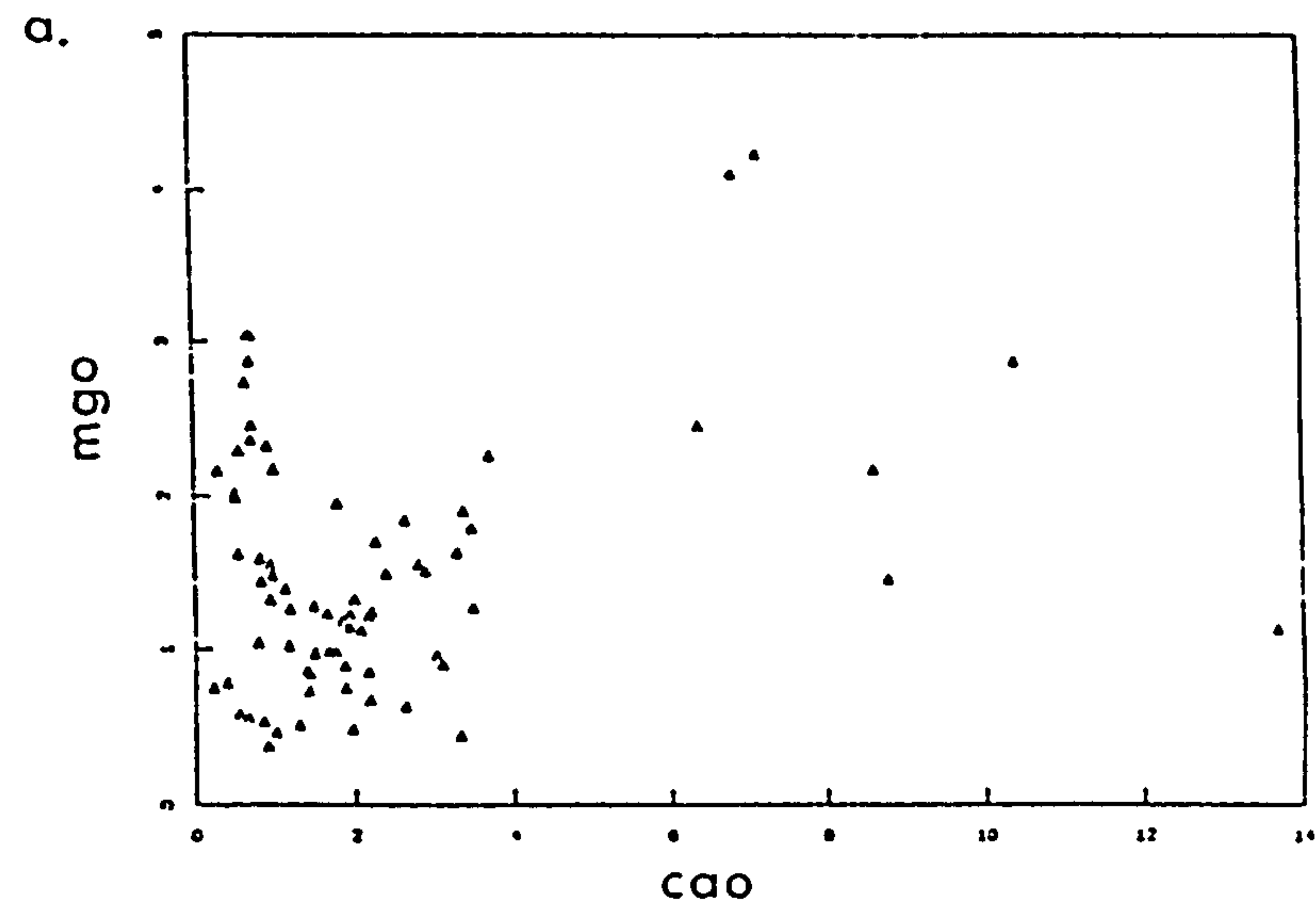


Fig. 5.2

Table 5.1.1

| | Total (CaCo3 free) | | | |
|-------|--------------------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO2 | 77.42 | 4.31 | 66.20 | 87.86 |
| TiO2 | 0.77 | 0.15 | 0.39 | 1.11 |
| Al2O3 | 9.64 | 1.52 | 5.71 | 13.27 |
| Fe2O3 | 1.79 | 0.77 | 0.23 | 3.77 |
| FeO | 2.32 | 0.85 | 0.21 | 4.00 |
| MnO | 0.07 | 0.05 | 0.00 | 0.57 |
| MgO | 2.12 | 0.82 | 0.37 | 4.97 |
| CaO | 0.26 | 0.34 | 0.00 | 1.89 |
| Na2O | 1.56 | 0.78 | 0.00 | 4.28 |
| K2O | 1.27 | 0.33 | 0.56 | 3.03 |
| P2O5 | 0.13 | 0.04 | 0.00 | 0.43 |
| H2O | 2.51 | 0.60 | 0.94 | 4.28 |
| CO2 | 0.14 | 0.37 | 0.00 | 2.44 |

Table 5.1.2

| | Straiton (CaCo3 free) | | | |
|-------|-----------------------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO2 | 80.07 | 4.33 | 68.24 | 87.86 |
| TiO2 | 0.76 | 0.13 | 0.40 | 1.05 |
| Al2O3 | 9.26 | 1.50 | 5.71 | 13.00 |
| Fe2O3 | 1.22 | 0.64 | 0.23 | 3.28 |
| FeO | 1.89 | 1.02 | 0.21 | 4.00 |
| MnO | 0.05 | 0.03 | 0.01 | 0.13 |
| MgO | 1.57 | 0.91 | 0.37 | 4.97 |
| CaO | 0.09 | 0.14 | 0.00 | 0.57 |
| Na2O | 0.93 | 0.58 | 0.00 | 2.12 |
| K2O | 1.30 | 0.25 | 0.69 | 1.88 |
| P2O5 | 0.14 | 0.05 | 0.05 | 0.43 |
| H2O | 2.37 | 0.72 | 1.10 | 4.28 |
| CO2 | 0.34 | 0.53 | 0.00 | 2.44 |

Table 5.1.3

| Hagshaw Hills (CaCo3 free) | | | | |
|--------------------------------|-------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO ₂ | 76.28 | 3.39 | 69.37 | 83.51 |
| TiO ₂ | 0.78 | 0.15 | 0.50 | 1.11 |
| Al ₂ O ₃ | 9.92 | 1.43 | 7.18 | 13.07 |
| Fe ₂ O ₃ | 2.21 | 0.69 | 0.80 | 3.75 |
| FeO | 2.27 | 0.57 | 1.41 | 3.33 |
| MnO | 0.10 | 0.06 | 0.04 | 0.27 |
| MgO | 2.10 | 0.45 | 1.16 | 2.91 |
| CaO | 0.26 | 0.32 | 0.00 | 1.89 |
| Na ₂ O | 1.77 | 0.59 | 0.70 | 3.16 |
| K ₂ O | 1.34 | 0.37 | 0.68 | 2.76 |
| P ₂ O ₅ | 0.13 | 0.03 | 0.08 | 0.22 |
| H ₂ O | 2.81 | 0.44 | 1.83 | 3.48 |
| CO ₂ | 0.04 | 0.18 | 0.00 | 1.18 |

Table 5.1.4

| Tinto (CaCo3 free) | | | | |
|--------------------------------|-------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO ₂ | 74.46 | 3.74 | 68.74 | 79.84 |
| TiO ₂ | 0.79 | 0.12 | 0.59 | 1.02 |
| Al ₂ O ₃ | 10.23 | 1.42 | 8.26 | 13.00 |
| Fe ₂ O ₃ | 1.91 | 0.60 | 1.04 | 3.40 |
| FeO | 2.79 | 0.81 | 1.22 | 4.00 |
| MnO | 0.08 | 0.02 | 0.05 | 0.12 |
| MgO | 2.85 | 0.70 | 1.94 | 4.44 |
| CaO | 0.63 | 0.45 | 0.04 | 1.46 |
| Na ₂ O | 2.20 | 0.45 | 1.56 | 3.20 |
| K ₂ O | 1.33 | 0.50 | 0.91 | 3.03 |
| P ₂ O ₅ | 0.13 | 0.05 | 0.08 | 0.28 |
| H ₂ O | 2.62 | 0.46 | 1.74 | 3.15 |
| CO ₂ | 0.00 | 0.00 | 0.00 | 0.00 |

Table 5.1.5

| | Carmichael (CaCo3 free) | | | |
|--------------------------------|-------------------------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO ₂ | 75.47 | 4.96 | 66.20 | 81.68 |
| TiO ₂ | 0.81 | 0.18 | 0.57 | 1.11 |
| Al ₂ O ₃ | 9.85 | 2.00 | 6.78 | 13.27 |
| Fe ₂ O ₃ | 2.46 | 0.54 | 1.73 | 3.50 |
| FeO | 2.49 | 0.65 | 1.37 | 3.27 |
| MnO | 0.06 | 0.01 | 0.04 | 0.07 |
| MgO | 2.29 | 0.51 | 1.67 | 3.06 |
| CaO | 0.69 | 0.49 | 0.00 | 1.55 |
| Na ₂ O | 2.16 | 1.02 | 1.35 | 4.28 |
| K ₂ O | 1.30 | 0.15 | 1.18 | 1.54 |
| P ₂ O ₅ | 0.12 | 0.05 | 0.05 | 0.20 |
| H ₂ O | 2.29 | 0.54 | 1.62 | 3.02 |
| CO ₂ | 0.01 | 0.03 | 0.00 | 0.08 |

Table 5.1.6

| North Esk (CaCo3 free) | | | | |
|--------------------------------|-------|--------|-------|-------|
| | mean | st.dev | min | max |
| SiO ₂ | 76.17 | 3.44 | 68.36 | 83.61 |
| TiO ₂ | 0.77 | 0.17 | 0.39 | 1.04 |
| Al ₂ O ₃ | 9.69 | 1.52 | 6.29 | 12.35 |
| Fe ₂ O ₃ | 2.05 | 0.62 | 0.84 | 3.77 |
| FeO | 2.71 | 0.56 | 1.54 | 3.77 |
| MnO | 0.08 | 0.07 | 0.00 | 0.57 |
| MgO | 2.55 | 0.52 | 1.41 | 3.75 |
| CaO | 0.31 | 0.34 | 0.00 | 1.78 |
| Na ₂ O | 1.90 | 0.68 | 0.09 | 3.38 |
| K ₂ O | 1.16 | 0.32 | 0.56 | 2.57 |
| P ₂ O ₅ | 0.11 | 0.04 | 0.00 | 0.22 |
| H ₂ O | 2.46 | 0.51 | 0.94 | 3.97 |
| CO ₂ | 0.03 | 0.10 | 0.00 | 0.57 |

| Table 5.1.7 (cont.) | | Statistical comparison of major oxides and trace elements from Greywacke Conglomerate | | | | |
|---------------------|----------------------------|---|-----------------------------|--------------|----------------------------|--------------|
| | Tinto-Carmichael | | Tinto-North Esk | | Carmichael-North Esk | |
| | F | t | F | t | F | t |
| SiO2 | <u>1.76</u> | <u>0.535</u> | <u>1.19</u> | <u>1.74</u> | <u>2.08</u> | <u>0.492</u> |
| TiO2 | <u>2.17</u> | <u>0.452</u> | <u>1.78</u> | <u>0.374</u> | <u>1.21</u> | <u>0.688</u> |
| Al2O3 | <u>1.99</u> | <u>0.512</u> | <u>1.15</u> | <u>1.27</u> | <u>1.73</u> | <u>0.257</u> |
| Fe2O3 | <u>1.23</u> | <u>2.08</u> | <u>1.06</u> | <u>0.835</u> | <u>1.31</u> | <u>1.67</u> |
| FeO | <u>1.56</u> | <u>0.854</u> | <u>2.06</u> | <u>0.446</u> | <u>1.32</u> | <u>0.965</u> |
| MnO | <u>3.01</u> | <u>2.27</u> | <u>12.20</u> | <u>0.365</u> | <u>36.78</u> | <u>0.934</u> |
| MgO | <u>1.90</u> | <u>1.90</u> | <u>1.82</u> | <u>1.88</u> | <u>1.05</u> | <u>1.29</u> |
| CaO | <u>1.18</u> | <u>0.295</u> | <u>1.73</u> | <u>3.13</u> | <u>2.04</u> | <u>2.68</u> |
| Na2O | <u>5.14</u> | <u>0.135</u> | <u>2.27</u> | <u>1.64</u> | <u>2.26</u> | <u>0.888</u> |
| K2O | <u>11.39</u> | <u>0.105</u> | <u>2.53</u> | <u>1.62</u> | <u>4.51</u> | <u>1.17</u> |
| P2O5 | <u>1.02</u> | <u>0.801</u> | <u>1.42</u> | <u>2.11</u> | <u>1.45</u> | <u>0.440</u> |
| H2O | <u>1.42</u> | <u>1.51</u> | <u>1.24</u> | <u>1.15</u> | <u>1.15</u> | <u>0.834</u> |
| Co2 | - | - | - | - | <u>11.46</u> | <u>0.351</u> |
| Co | <u>1.85</u> | <u>0.80</u> | <u>2.75</u> | <u>0.898</u> | <u>1.48</u> | <u>0.018</u> |
| Cr | <u>28.59</u> | <u>2.80</u> | <u>14.50</u> | <u>0.639</u> | <u>1.97</u> | <u>2.00</u> |
| Ce | <u>5.72</u> | <u>2.48</u> | <u>2.62</u> | <u>1.73</u> | <u>2.18</u> | <u>3.63</u> |
| Ba | <u>3.68</u> | <u>0.938</u> | <u>2.65</u> | <u>2.09</u> | <u>1.39</u> | <u>0.137</u> |
| La | <u>1.94</u> | <u>2.30</u> | <u>1.06</u> | <u>0.292</u> | <u>2.04</u> | <u>2.21</u> |
| Zr | <u>5.12</u> | <u>1.65</u> | <u>2.80</u> | <u>0.382</u> | <u>1.83</u> | <u>1.35</u> |
| Y | <u>1.23</u> | <u>0.586</u> | <u>1.23</u> | <u>0.578</u> | <u>1.52</u> | <u>1.15</u> |
| Sr | <u>2.92</u> | <u>0.673</u> | <u>1.30</u> | <u>3.44</u> | <u>3.80</u> | <u>1.25</u> |
| U | <u>4.48</u> | <u>0.519</u> | <u>2.12</u> | <u>0.286</u> | <u>2.12</u> | <u>0.550</u> |
| Rb | <u>7.13</u> | <u>0.204</u> | <u>3.44</u> | <u>1.74</u> | <u>2.07</u> | <u>1.13</u> |
| Th | <u>2.69</u> | <u>0.369</u> | <u>2.06</u> | <u>2.80</u> | <u>1.31</u> | <u>1.63</u> |
| Pb | <u>10.65</u> | <u>0.550</u> | <u>16.79</u> | <u>2.72</u> | <u>1.58</u> | <u>1.60</u> |
| Ga | <u>1.28</u> | <u>0.878</u> | <u>1.37</u> | <u>1.96</u> | <u>1.08</u> | <u>0.456</u> |
| Zn | <u>1.32</u> | <u>0.856</u> | <u>1.32</u> | <u>0.840</u> | <u>1.00</u> | <u>0.473</u> |
| Cu | <u>1.57</u> | <u>0.498</u> | <u>2.73</u> | <u>0.973</u> | <u>1.74</u> | <u>0.276</u> |
| Ni | <u>9.84</u> | <u>1.31</u> | <u>4.34</u> | <u>0.722</u> | <u>2.27</u> | <u>0.830</u> |
| Nb | <u>1.89</u> | <u>0.169</u> | <u>1.44</u> | <u>1.21</u> | <u>1.31</u> | <u>0.633</u> |
| | <u>F(15, 6; 0.05)=3.93</u> | | <u>F(63, 15; 0.05)=2.16</u> | | <u>F(6, 63; 0.05)=2.25</u> | |
| | <u>F(6, 15; 0.05)=2.80</u> | | <u>F(15, 63; 0.05)=1.83</u> | | <u>F(63, 6; 0.05)=3.74</u> | |
| | <u>t(0.05/2; 21)=±2.08</u> | | <u>t(0.05/2; 78)=±1.99</u> | | <u>t(0.05/2; 69)=±1.97</u> | |

| Table 5.1.7 (cont.) | | Statistical comparison of major oxides and trace elements from Greywacke Conglomerate | | | | |
|---------------------|----------------------------|---|----------------------------|--------------|-----------------------------|--------------|
| | Hagshaw Hills-Tinto | | Hagshaw Hills-Carmichael | | Hagshaw Hills-North Esk | |
| | F | t | F | t | F | t |
| SiO2 | <u>1.22</u> | <u>1.78</u> | <u>2.15</u> | <u>0.551</u> | <u>1.03</u> | <u>0.159</u> |
| TiO2 | <u>1.52</u> | <u>0.219</u> | <u>1.43</u> | <u>0.607</u> | <u>1.18</u> | <u>0.230</u> |
| Al2O3 | <u>1.02</u> | <u>0.744</u> | <u>1.95</u> | <u>0.102</u> | <u>1.13</u> | <u>0.766</u> |
| Fe2O3 | <u>1.30</u> | <u>1.53</u> | <u>1.60</u> | <u>0.937</u> | <u>1.22</u> | <u>1.21</u> |
| FeO | <u>2.02</u> | <u>2.77</u> | <u>1.30</u> | <u>0.943</u> | <u>1.02</u> | <u>3.99</u> |
| MnO | <u>9.40</u> | <u>1.35</u> | <u>28.34</u> | <u>1.69</u> | <u>1.35</u> | <u>4.71</u> |
| MgO | <u>2.45</u> | <u>4.88</u> | <u>1.29</u> | <u>1.01</u> | <u>1.30</u> | <u>1.13</u> |
| CaO | <u>2.00</u> | <u>3.60</u> | <u>2.35</u> | <u>3.12</u> | <u>1.16</u> | <u>0.854</u> |
| Na2O | <u>1.70</u> | <u>2.64</u> | <u>3.02</u> | <u>1.45</u> | <u>1.34</u> | <u>1.07</u> |
| K2O | <u>1.87</u> | <u>0.114</u> | <u>6.11</u> | <u>0.241</u> | <u>1.35</u> | <u>2.66</u> |
| P2O5 | <u>1.92</u> | <u>0.287</u> | <u>1.96</u> | <u>0.957</u> | <u>1.35</u> | <u>2.88</u> |
| H2O | <u>1.07</u> | <u>1.46</u> | <u>1.52</u> | <u>2.81</u> | <u>3.17</u> | <u>3.71</u> |
| Co2 | - | - | - | - | <u>1.57</u> | <u>0.548</u> |
| Co | <u>1.55</u> | <u>1.11</u> | <u>1.19</u> | <u>1.53</u> | <u>1.77</u> | <u>2.63</u> |
| Cr | <u>1.78</u> | <u>1.81</u> | <u>16.04</u> | <u>4.85</u> | <u>8.14</u> | <u>2.14</u> |
| Ce | <u>3.31</u> | <u>0.933</u> | <u>1.73</u> | <u>1.65</u> | <u>1.25</u> | <u>3.54</u> |
| Ba | <u>16.94</u> | <u>2.46</u> | <u>4.60</u> | <u>0.143</u> | <u>6.40</u> | <u>0.166</u> |
| La | <u>1.13</u> | <u>2.91</u> | <u>2.19</u> | <u>0.186</u> | <u>1.07</u> | <u>3.95</u> |
| Zr | <u>3.47</u> | <u>2.70</u> | <u>1.48</u> | <u>0.289</u> | <u>1.24</u> | <u>3.38</u> |
| Y | <u>1.54</u> | <u>0.285</u> | <u>1.24</u> | <u>0.353</u> | <u>1.89</u> | <u>1.20</u> |
| Sr | <u>1.82</u> | <u>3.37</u> | <u>5.30</u> | <u>1.13</u> | <u>1.40</u> | <u>0.399</u> |
| U | <u>2.25</u> | <u>0.491</u> | <u>2.00</u> | <u>1.21</u> | <u>1.06</u> | <u>1.28</u> |
| Rb | <u>2.32</u> | <u>0.341</u> | <u>3.08</u> | <u>0.018</u> | <u>1.49</u> | <u>2.09</u> |
| Th | <u>1.15</u> | <u>3.13</u> | <u>2.35</u> | <u>1.96</u> | <u>1.80</u> | <u>1.72</u> |
| Pb | <u>51.48</u> | <u>3.85</u> | <u>4.83</u> | <u>5.42</u> | <u>3.07</u> | <u>5.24</u> |
| Ga | <u>1.07</u> | <u>0.125</u> | <u>1.37</u> | <u>1.12</u> | <u>1.47</u> | <u>3.09</u> |
| Zn | <u>2.29</u> | <u>6.70</u> | <u>1.74</u> | <u>4.22</u> | <u>1.73</u> | <u>8.70</u> |
| Cu | <u>1.46</u> | <u>1.70</u> | <u>2.29</u> | <u>1.87</u> | <u>3.97</u> | <u>3.17</u> |
| Ni | <u>1.77</u> | <u>1.31</u> | <u>5.55</u> | <u>2.35</u> | <u>2.58</u> | <u>2.45</u> |
| Nb | <u>1.77</u> | <u>0.884</u> | <u>1.07</u> | <u>0.437</u> | <u>1.23</u> | <u>0.282</u> |
| | <u>F(43,15; 0.05)=2.20</u> | | <u>F(43,6; 0.05)=3.77</u> | | <u>F(43,63; 0.05)=1.57</u> | |
| | <u>F(15,43; 0.05)=1.91</u> | | <u>F(6,43; 0.05)=2.32</u> | | <u>F(63,43; 0.05)=1.61</u> | |
| | <u>t(0.05/2; 58)=±2.00</u> | | <u>t(0.05/2; 49)=±2.01</u> | | <u>t(0.05/2; 106)=±1.98</u> | |

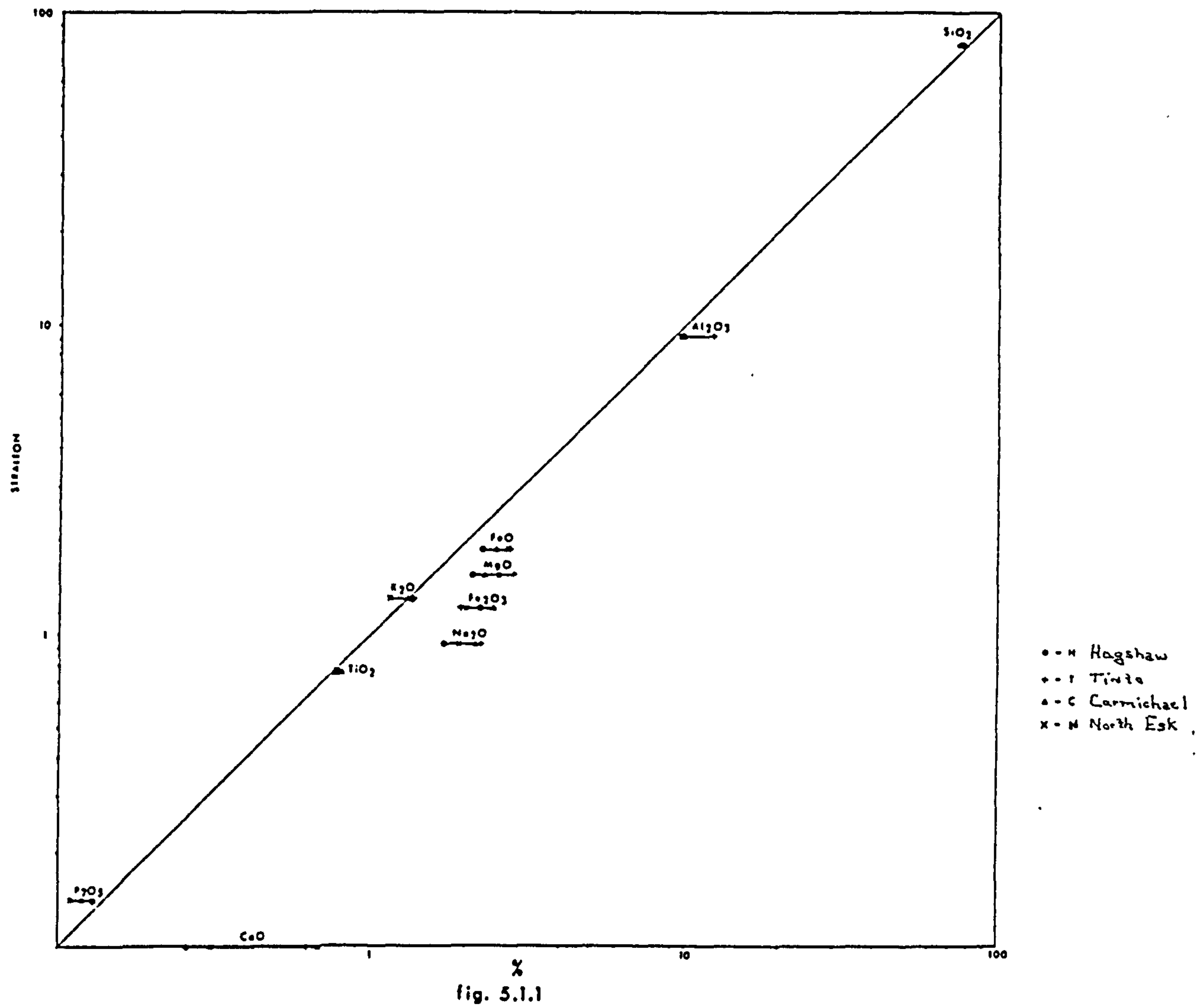


Fig. 5.1.1 Comparison of major oxide means between Straiton and Hagshaw Hills, Tinto/Carmichael, and North Esk sandstone clasts.

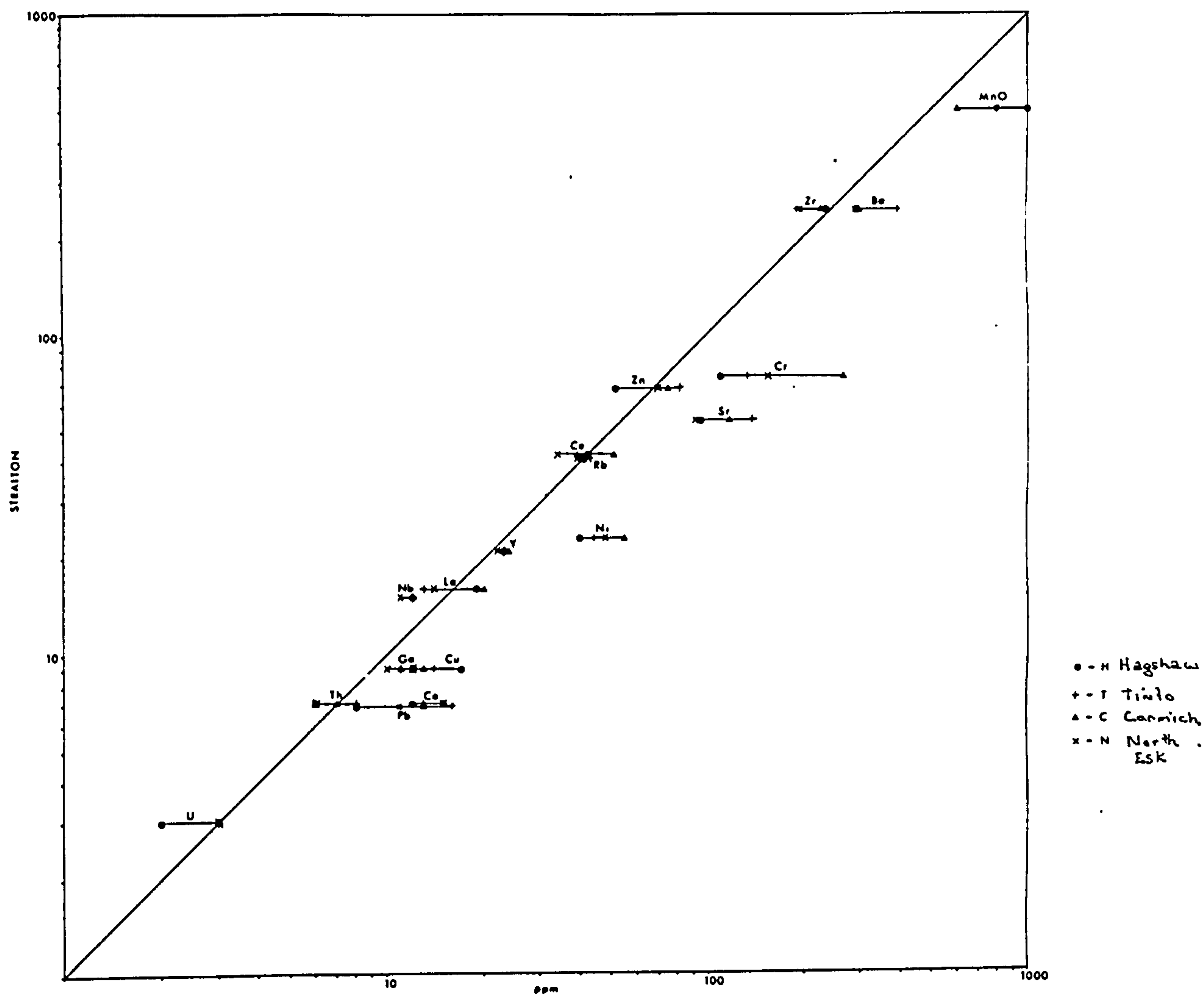
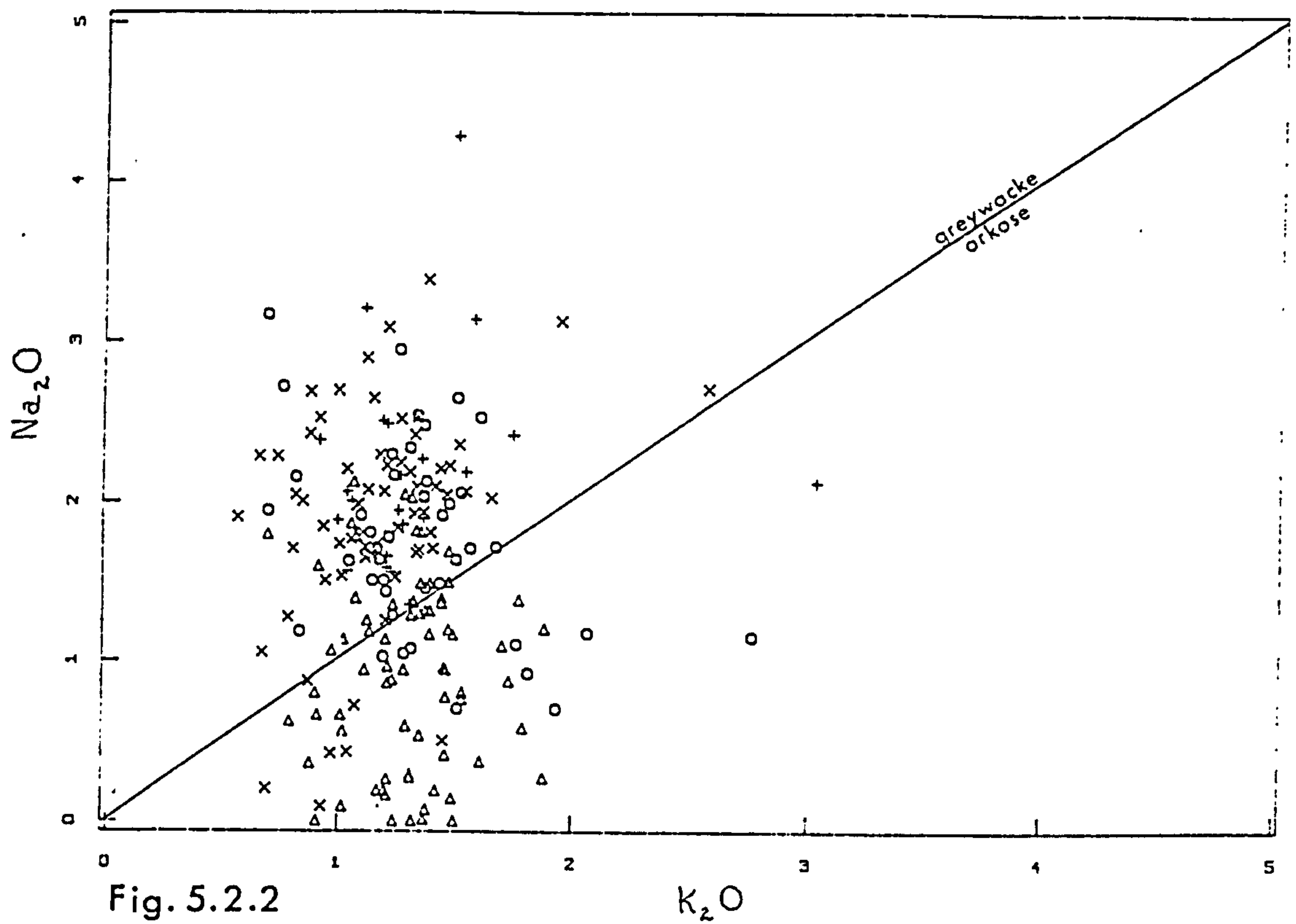
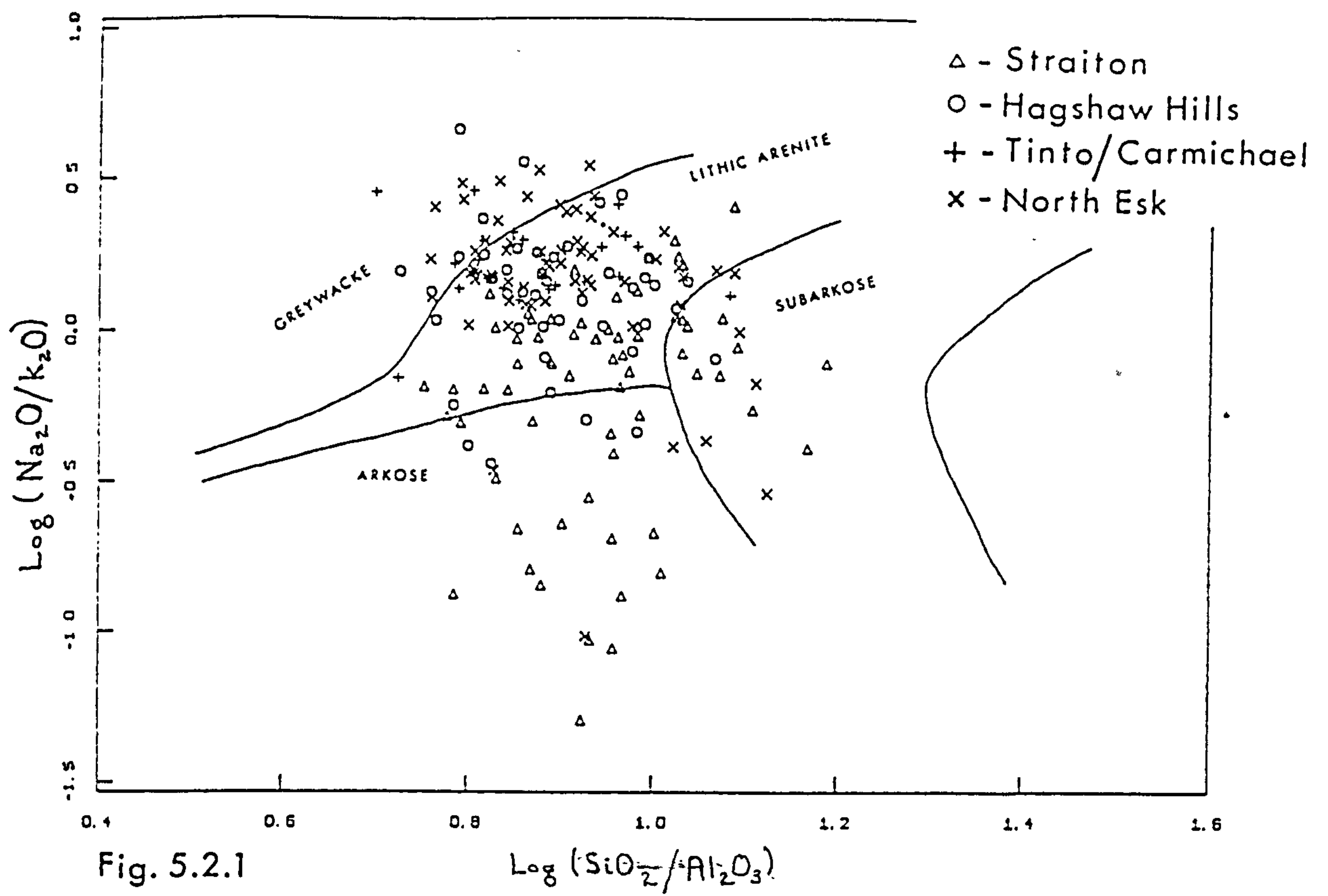


fig. 5.1.2

Fig. 5.1.2 Comparison of trace element means between Straiton and Hagshaw Hills, Tinto/Carmichael, and North Esk sandstone clasts.



Figs. 5.2.1 and 5.2.2 Chemical classification of Greywacke conglomerate sandstone clasts.

Table 5.3.1

Correlation Matrix for Straiton

| | SiO2 | TiO2 | Al2O3 | Fe2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | P2O5 | H2O | Co2 | co | cr |
|-------|--------|-------|-------|-------|--------|--------|--------|--------|--------|-------|-------|-------|--------|-------|-------|
| SiO2 | 1.000 | | | | | | | | | | | | | | |
| TiO2 | -0.409 | 1.000 | | | | | | | | | | | | | |
| Al2O3 | -0.810 | 0.474 | 1.000 | | | | | | | | | | | | |
| Fe2O3 | -0.738 | 0.454 | 0.554 | 1.000 | | | | | | | | | | | |
| FeO | -0.701 | | 0.404 | 0.444 | 1.000 | | | | | | | | | | |
| MnO | -0.413 | | | 0.382 | 0.254 | 1.000 | | | | | | | | | |
| MgO | -0.797 | | 0.420 | 0.508 | 0.871 | 0.504 | 1.000 | | | | | | | | |
| CaO | | | | | -0.298 | | | 1.000 | | | | | | | |
| Na2O | | | | | 0.298 | | | -0.311 | 1.000 | | | | | | |
| K2O | -0.614 | 0.460 | 0.773 | 0.509 | 0.307 | 0.322 | 0.373 | | | 1.000 | | | | | |
| P2O5 | -0.304 | 0.494 | 0.366 | | | | | | | 0.326 | 1.000 | | | | |
| H2O | -0.699 | 0.288 | 0.651 | 0.596 | 0.255 | 0.520 | 0.407 | | -0.314 | 0.516 | | 1.000 | | | |
| Co2 | -0.381 | | | 0.295 | 0.388 | 0.434 | 0.407 | -0.478 | | 0.291 | | 0.255 | 1.000 | | |
| co | -0.646 | | 0.533 | 0.550 | 0.519 | 0.270 | 0.511 | -0.244 | | 0.385 | | 0.621 | 0.260 | 1.000 | |
| cr | -0.453 | | 0.378 | 0.360 | 0.284 | | 0.333 | -0.271 | | | | 0.321 | | 0.346 | 1.000 |
| ce | | | | | | | -0.235 | | | | | | | | |
| ba | -0.409 | 0.374 | 0.639 | 0.349 | | | | -0.272 | | 0.747 | | 0.396 | | 0.451 | 0.251 |
| la | | | | | | | | | | | | | | | |
| zr | | 0.666 | | | | -0.263 | | | | | 0.387 | | | | |
| y | | 0.467 | | 0.315 | | | | | | 0.269 | 0.502 | | 0.278 | | |
| sr | -0.324 | | 0.272 | | 0.386 | 0.234 | 0.283 | | | 0.257 | | | 0.270 | 0.235 | |
| u | | 0.297 | | | | | | | -0.275 | | | | | | |
| rb | -0.400 | 0.393 | 0.678 | 0.290 | | | | | | 0.850 | 0.248 | 0.351 | | 0.298 | |
| th | -0.245 | 0.507 | 0.356 | 0.324 | 0.275 | | | | | 0.410 | 0.250 | | | | |
| pb | -0.314 | 0.313 | 0.396 | 0.302 | | 0.257 | | | | 0.404 | | 0.479 | | 0.397 | |
| ga | -0.593 | 0.397 | 0.738 | 0.410 | 0.335 | | 0.339 | | | 0.606 | | 0.488 | | 0.498 | 0.333 |
| zn | -0.317 | | 0.339 | | 0.307 | | 0.260 | | | 0.333 | | | | 0.355 | 0.508 |
| cu | | 0.285 | | 0.252 | | | | | 0.331 | | | | | | 0.343 |
| ni | -0.662 | | 0.535 | 0.632 | 0.600 | | 0.568 | | | 0.348 | | 0.605 | | 0.749 | 0.463 |
| rb | | 0.474 | 0.312 | | | -0.268 | -0.265 | | | 0.337 | 0.427 | | -0.287 | | |

| Table 5.3.1 (cont.) | | Correlation matrix for Straiton | | | | | | | | | | | | | |
|---------------------|-------|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | ce | ba | la | zr | y | sr | u | rb | th | pb | ga | zn | cu | ni | rb |
| SiO2 | | | | | | | | | | | | | | | |
| TiO2 | | | | | | | | | | | | | | | |
| Al2O3 | | | | | | | | | | | | | | | |
| Fe2O3 | | | | | | | | | | | | | | | |
| FeO | | | | | | | | | | | | | | | |
| MnO | | | | | | | | | | | | | | | |
| MgO | | | | | | | | | | | | | | | |
| CaO | | | | | | | | | | | | | | | |
| Na2O | | | | | | | | | | | | | | | |
| K2O | | | | | | | | | | | | | | | |
| P2O5 | | | | | | | | | | | | | | | |
| H2O | | | | | | | | | | | | | | | |
| Co2 | | | | | | | | | | | | | | | |
| ∞ | | | | | | | | | | | | | | | |
| cr | | | | | | | | | | | | | | | |
| ce | 1.000 | | | | | | | | | | | | | | |
| ba | | 1.000 | | | | | | | | | | | | | |
| la | 0.862 | | 1.000 | | | | | | | | | | | | |
| zr | 0.405 | | 0.358 | 1.000 | | | | | | | | | | | |
| y | 0.727 | | 0.668 | 0.536 | 1.000 | | | | | | | | | | |
| sr | 0.380 | | | | 0.348 | 1.000 | | | | | | | | | |
| u | | | | 0.265 | | | 1.000 | | | | | | | | |
| rb | | 0.801 | | | | | | 1.000 | | | | | | | |
| th | | 0.382 | | 0.436 | 0.305 | | | 0.465 | 1.000 | | | | | | |
| pb | | 0.426 | | | | | | 0.386 | 0.387 | 1.000 | | | | | |
| ga | | 0.703 | | | | | | 0.711 | 0.377 | 0.373 | 1.000 | | | | |
| zn | | 0.400 | | | | | | 0.379 | | | 0.332 | 1.000 | | | |
| cu | | | | | | | | | | | | | 1.000 | | |
| ni | | 0.369 | | | | | | 0.260 | 0.331 | 0.354 | 0.538 | | | 1.000 | |
| rb | 0.240 | 0.325 | | 0.431 | 0.234 | | | 0.451 | 0.288 | | 0.350 | | | | 1.000 |

Table 5.3.2

Correlation matrix for Hagshaw Hills, Carmichael, Tinto and North Esk

| | SiO2 | TiO2 | Al2O3 | Fe2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | P2O5 | H2O | Co2 | ∞ | α |
|-------|--------|-------|-------|-------|--------|--------|-------|--------|--------|--------|-------|-------|-------|-------|--------|
| SiO2 | 1.000 | | | | | | | | | | | | | | |
| TiO2 | -0.607 | 1.000 | | | | | | | | | | | | | |
| Al2O3 | -0.919 | 0.514 | 1.000 | | | | | | | | | | | | |
| Fe2O3 | -0.573 | 0.436 | 0.383 | 1.000 | | | | | | | | | | | |
| FeO | -0.532 | 0.668 | 0.455 | | 1.000 | | | | | | | | | | |
| MnO | -0.243 | | 0.199 | | | 1.000 | | | | | | | | | |
| MgO | -0.679 | 0.393 | 0.447 | 0.542 | 0.399 | | 1.000 | | | | | | | | |
| CaO | -0.159 | | | | 0.143 | | | 1.000 | | | | | | | |
| Na2O | -0.452 | 0.162 | 0.475 | | 0.199 | | 0.227 | | 1.000 | | | | | | |
| K2O | -0.356 | | 0.472 | | -0.174 | 0.176 | | | | 1.000 | | | | | |
| P2O5 | -0.430 | 0.332 | 0.465 | | 0.272 | 0.225 | 0.210 | 0.145 | 0.257 | 0.186 | 1.000 | | | | |
| H2O | -0.549 | 0.427 | 0.448 | 0.440 | 0.268 | 0.197 | 0.389 | | -0.162 | 0.151 | 0.238 | 1.000 | | | |
| Co2 | -0.253 | | 0.231 | 0.189 | | 0.153 | 0.158 | -0.361 | | | 0.217 | | 1.000 | | |
| Co | -0.424 | 0.479 | 0.231 | 0.493 | 0.489 | | 0.572 | | | -0.159 | | 0.366 | | 1.000 | |
| Cr | | | | 0.378 | | | 0.535 | | | | | | | 0.248 | 1.000 |
| Ce | -0.258 | 0.320 | 0.252 | 0.183 | | | | | | | 0.288 | 0.295 | 0.284 | | |
| Ba | -0.446 | 0.197 | 0.466 | 0.192 | | | 0.138 | | | 0.488 | 0.187 | 0.249 | 0.209 | | -0.208 |
| La | | 0.141 | | 0.153 | | | | | | | 0.232 | 0.142 | 0.148 | | |
| Zr | -0.212 | 0.656 | 0.218 | 0.197 | 0.202 | | | | | 0.216 | 0.208 | 0.315 | | 0.246 | |
| Y | -0.486 | 0.519 | 0.431 | 0.331 | 0.325 | 0.184 | 0.295 | 0.138 | 0.163 | | 0.419 | 0.299 | 0.221 | 0.340 | |
| Sr | -0.559 | | 0.543 | | | 0.260 | 0.280 | 0.252 | 0.623 | 0.144 | 0.331 | | 0.300 | | |
| U | | | | 0.165 | | -0.154 | 0.191 | | | | | 0.178 | | 0.182 | 0.141 |
| Rb | -0.331 | 0.148 | 0.459 | | | | | | | 0.884 | 0.142 | 0.185 | | | |
| Th | -0.304 | 0.210 | 0.267 | | 0.138 | | 0.265 | | | 0.418 | 0.240 | | | | 0.184 |
| Pb | -0.207 | 0.239 | | 0.229 | 0.192 | | 0.413 | | 0.247 | | | | | 0.224 | 0.236 |
| Ga | -0.717 | 0.584 | 0.760 | 0.410 | 0.379 | | 0.335 | | 0.219 | 0.351 | 0.364 | 0.497 | 0.190 | 0.365 | |
| Zn | -0.549 | 0.407 | 0.395 | 0.390 | 0.522 | -0.147 | 0.759 | | 0.276 | | | | | 0.572 | 0.413 |
| Cu | -0.254 | 0.183 | 0.270 | 0.175 | | | | | 0.226 | | 0.337 | 0.310 | 0.238 | | |
| Ni | -0.260 | 0.224 | | 0.415 | 0.194 | | 0.665 | | | | | 0.259 | | 0.498 | 0.781 |
| Nb | -0.328 | 0.570 | 0.332 | | 0.283 | | | | 0.285 | 0.267 | 0.245 | | | | |

| Table 5.3.2 (cont.) Correlation Matrix for Hagshaw Hills, Carmichael, Tinto, and North Esk | | | | | | | | | | | | | | | |
|--|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|
| | ce | ba | la | zr | y | sr | u | rb | th | pb | ga | zn | cu | ni | rb |
| SiO2 | | | | | | | | | | | | | | | |
| TiO2 | | | | | | | | | | | | | | | |
| Al2O3 | | | | | | | | | | | | | | | |
| Fe2O3 | | | | | | | | | | | | | | | |
| FeO | | | | | | | | | | | | | | | |
| MnO | | | | | | | | | | | | | | | |
| MgO | | | | | | | | | | | | | | | |
| CaO | | | | | | | | | | | | | | | |
| Na2O | | | | | | | | | | | | | | | |
| K2O | | | | | | | | | | | | | | | |
| P2O5 | | | | | | | | | | | | | | | |
| H2O | | | | | | | | | | | | | | | |
| Co2 | | | | | | | | | | | | | | | |
| co | | | | | | | | | | | | | | | |
| cr | | | | | | | | | | | | | | | |
| ce | 1.000 | | | | | | | | | | | | | | |
| ba | 0.252 | 1.000 | | | | | | | | | | | | | |
| la | 0.729 | 0.148 | 1.000 | | | | | | | | | | | | |
| zr | 0.404 | 0.206 | 0.302 | 1.000 | | | | | | | | | | | |
| y | 0.538 | 0.293 | 0.459 | 0.430 | 1.000 | | | | | | | | | | |
| sr | 0.245 | 0.385 | | -0.152 | 0.304 | 1.000 | | | | | | | | | |
| u | | | | | | | 1.000 | | | | | | | | |
| rb | | 0.417 | | 0.366 | | | 0.171 | 1.000 | | | | | | | |
| th | 0.179 | 0.303 | | 0.341 | 0.236 | | 0.249 | 0.508 | 1.000 | | | | | | |
| pb | | 0.170 | | | 0.188 | | | | 0.290 | 1.000 | | | | | |
| ga | 0.329 | 0.446 | 0.165 | 0.449 | 0.446 | 0.297 | | 0.432 | 0.301 | | 1.000 | | | | |
| zn | | | | | 0.210 | | 0.202 | | 0.354 | 0.536 | 0.285 | 1.000 | | | |
| cu | 0.306 | 0.298 | 0.269 | | 0.303 | 0.379 | | | | | 0.390 | -0.175 | 1.000 | | |
| ni | | | | | | | 0.196 | | 0.151 | 0.247 | 0.145 | 0.489 | | 1.000 | |
| rb | | 0.231 | | 0.517 | 0.197 | | | 0.428 | 0.378 | 0.201 | 0.406 | 0.308 | | | 1.000 |

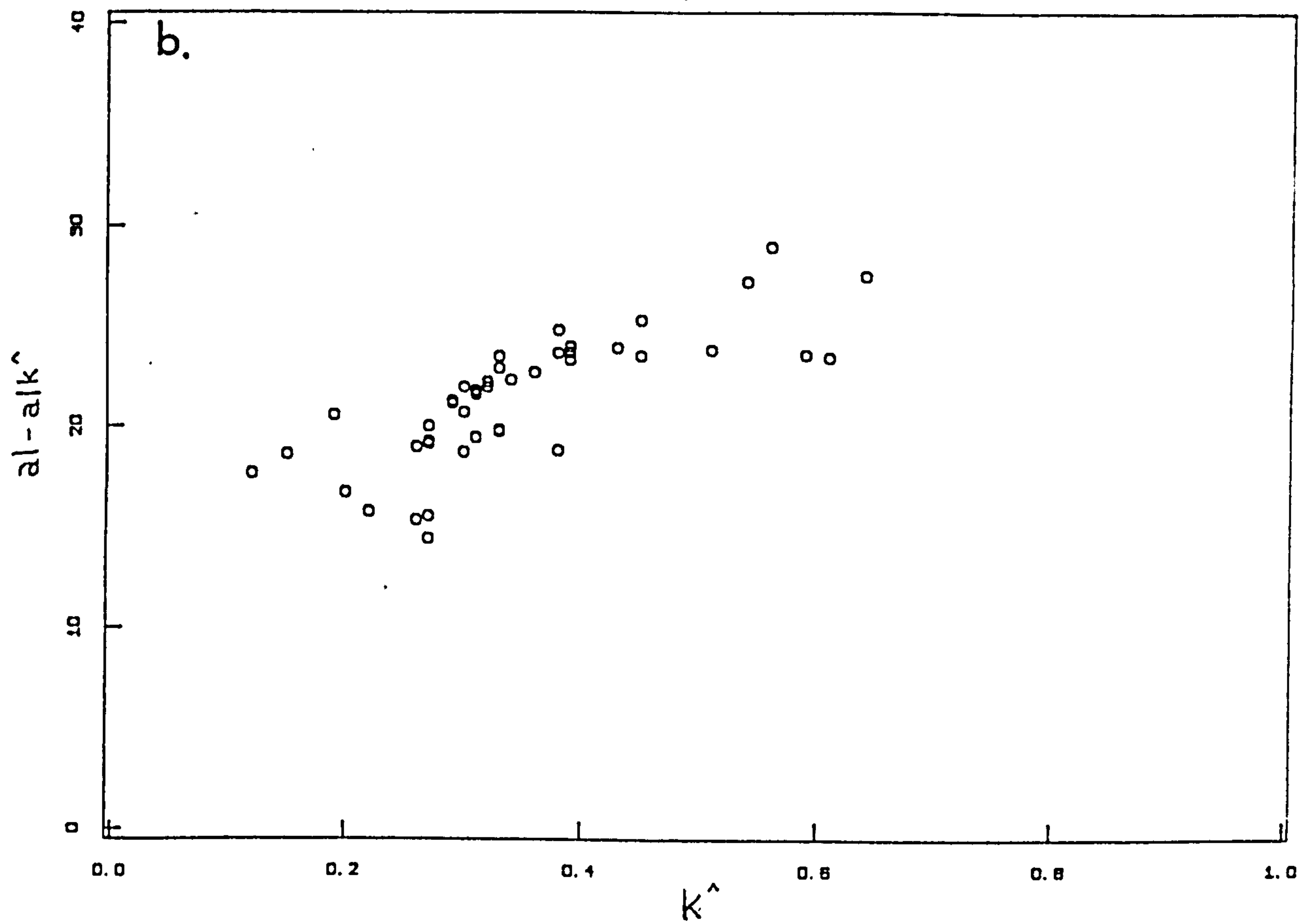
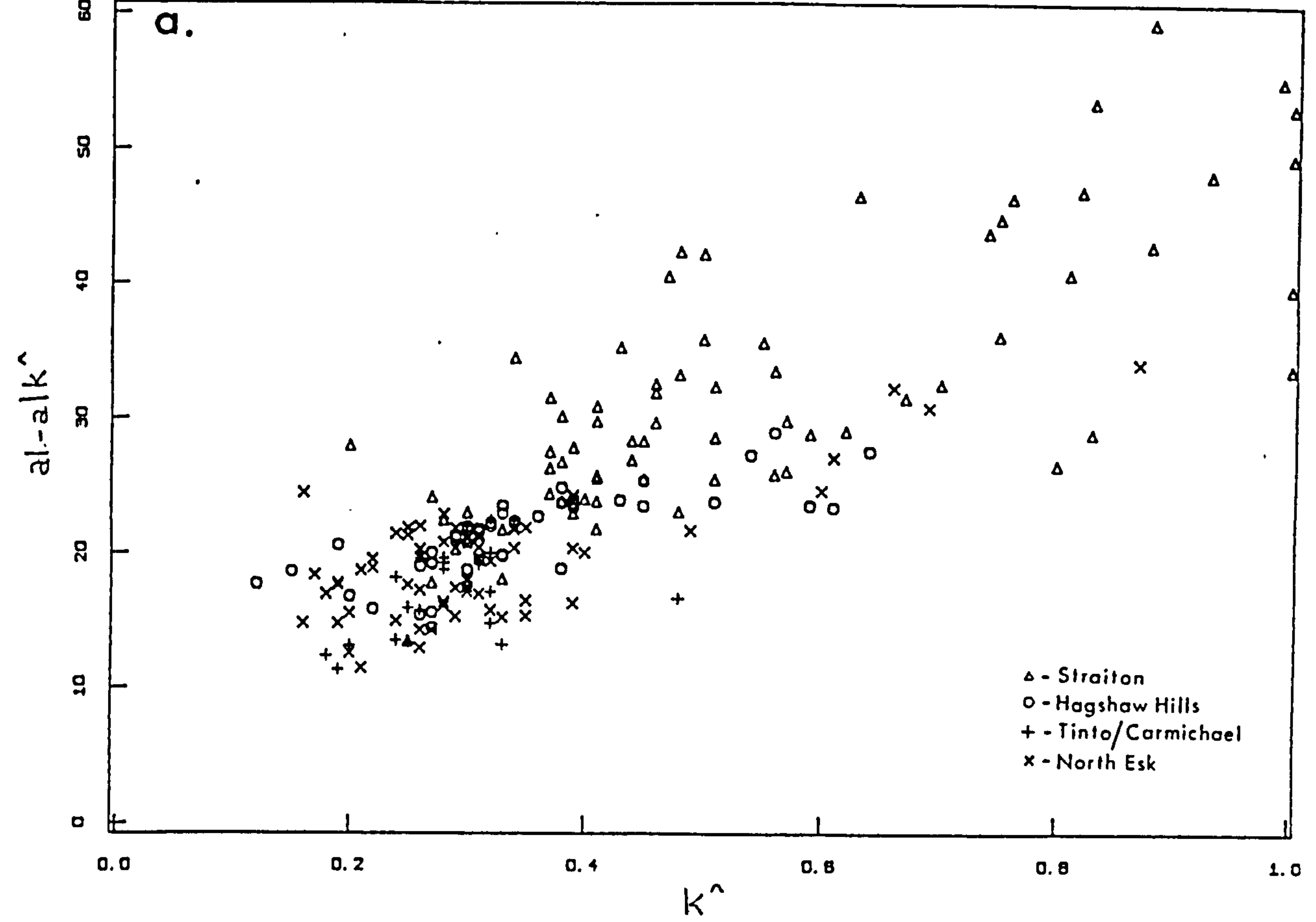


Fig. 5.3.1 (a-b) k^{\wedge} vs $al^{\wedge}-alk^{\wedge}$

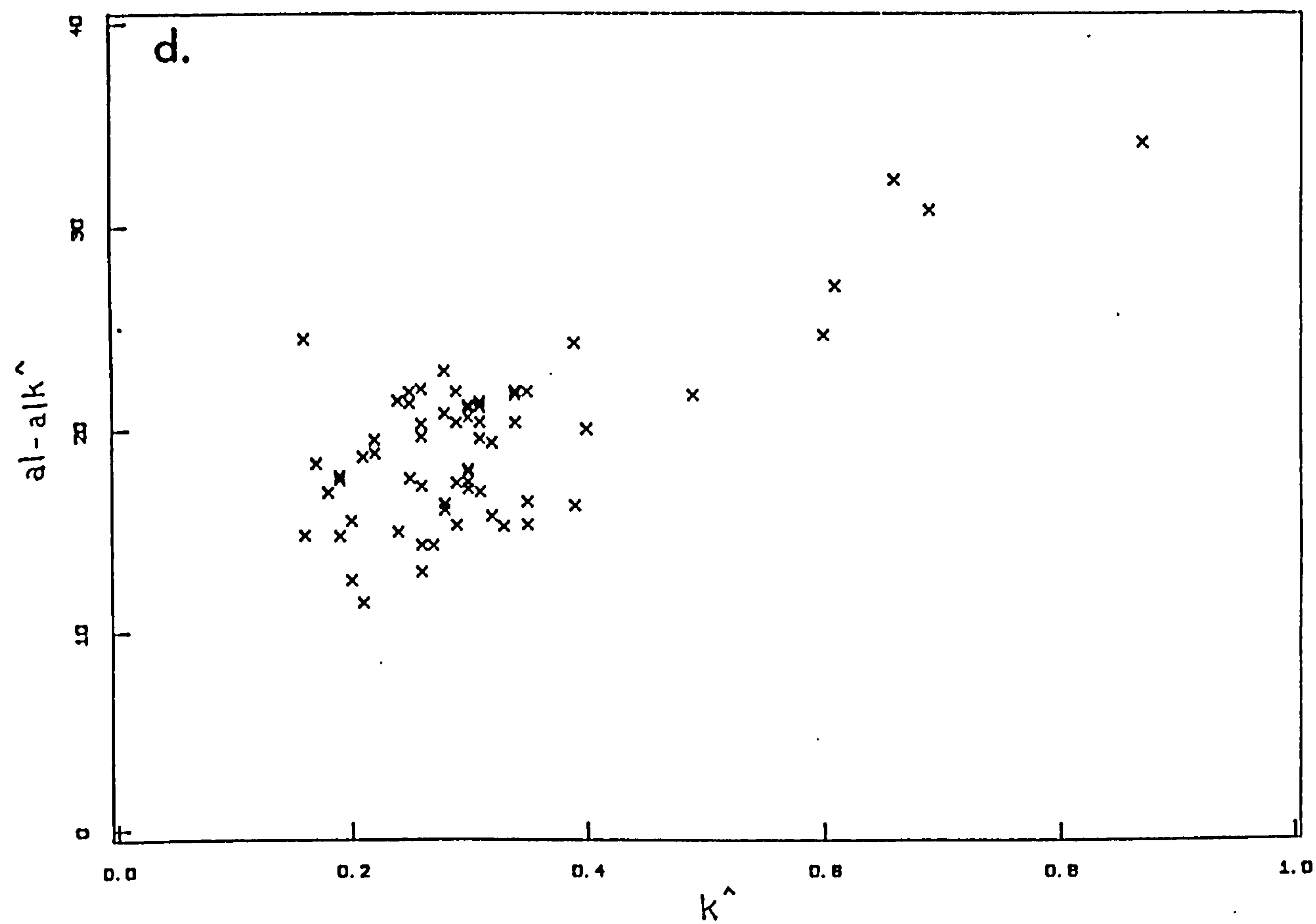
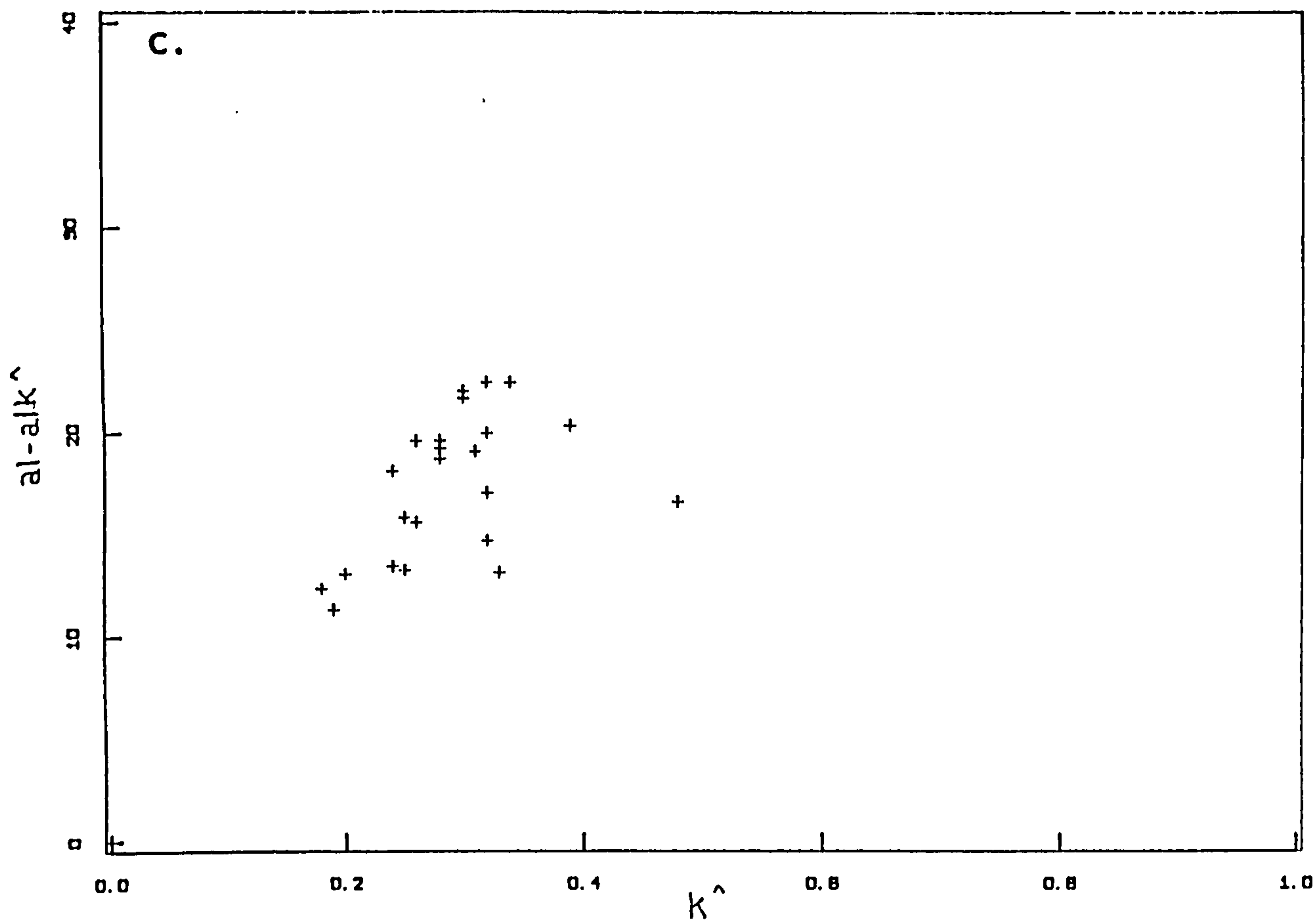


Fig. 5.3.1 (c-d) $k^$ vs $al-alk^$

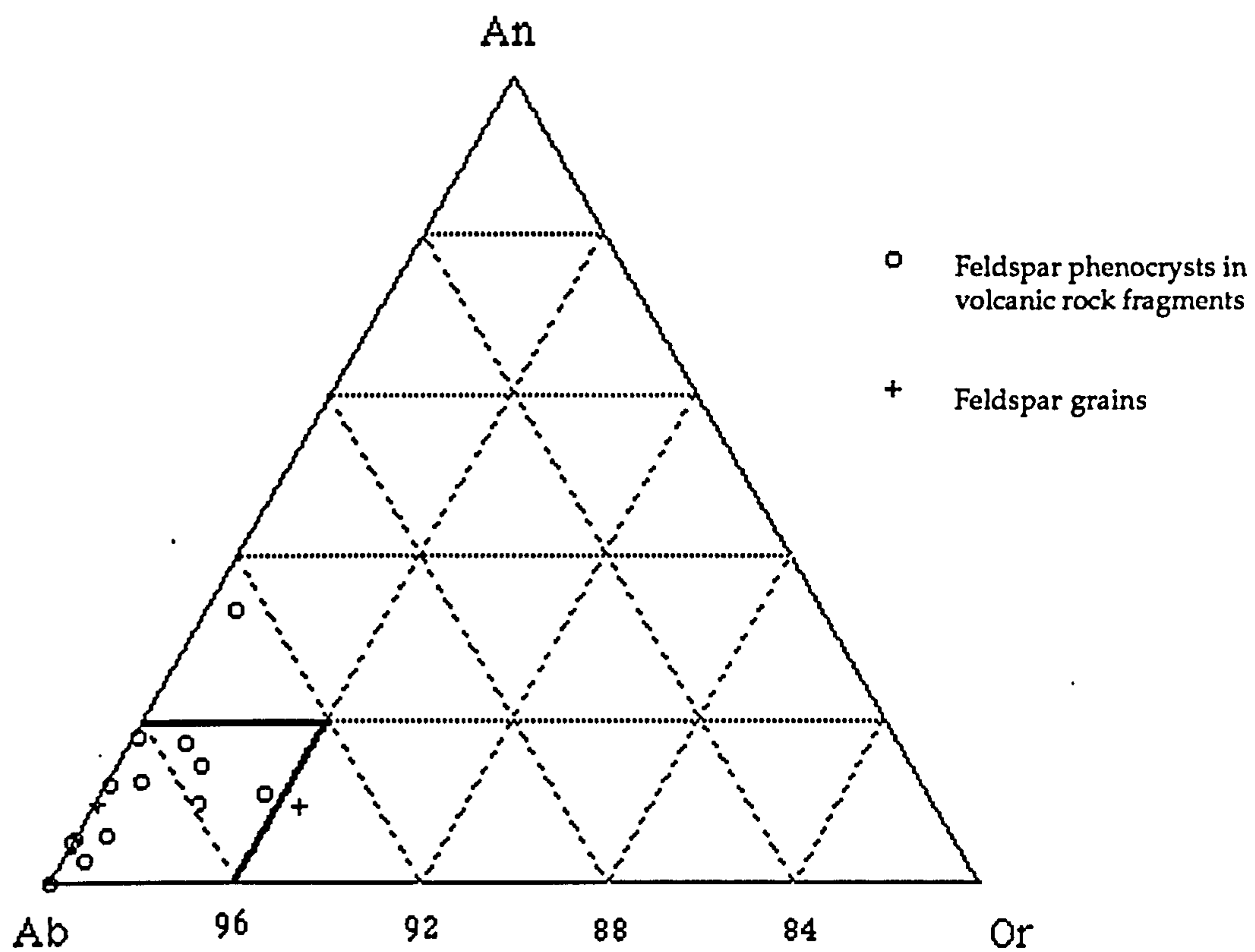


Fig. 5.3.2 Feldspar composition in sandstone clast, sample from Hagshaw Hills

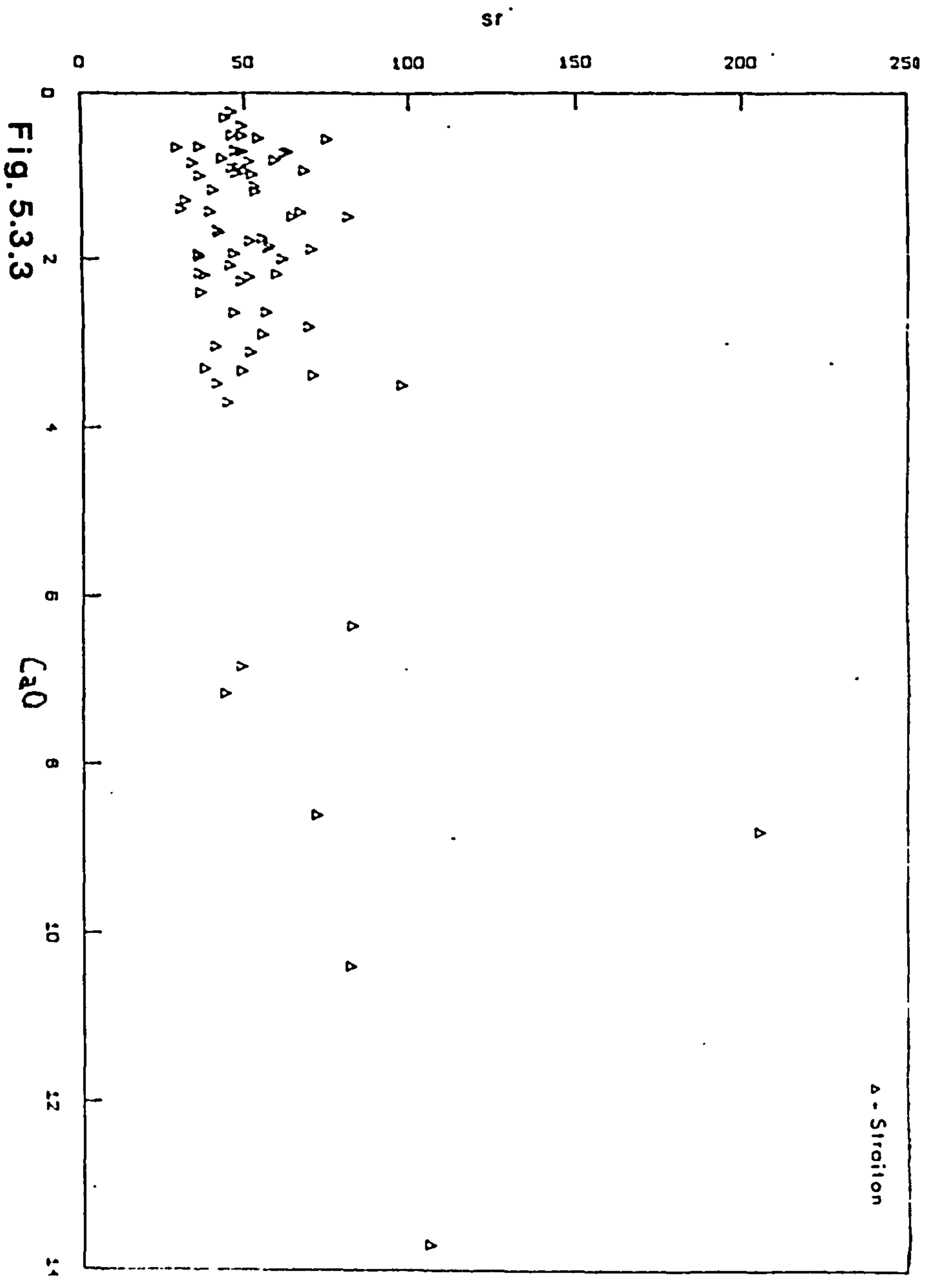


Fig. 5.3.3

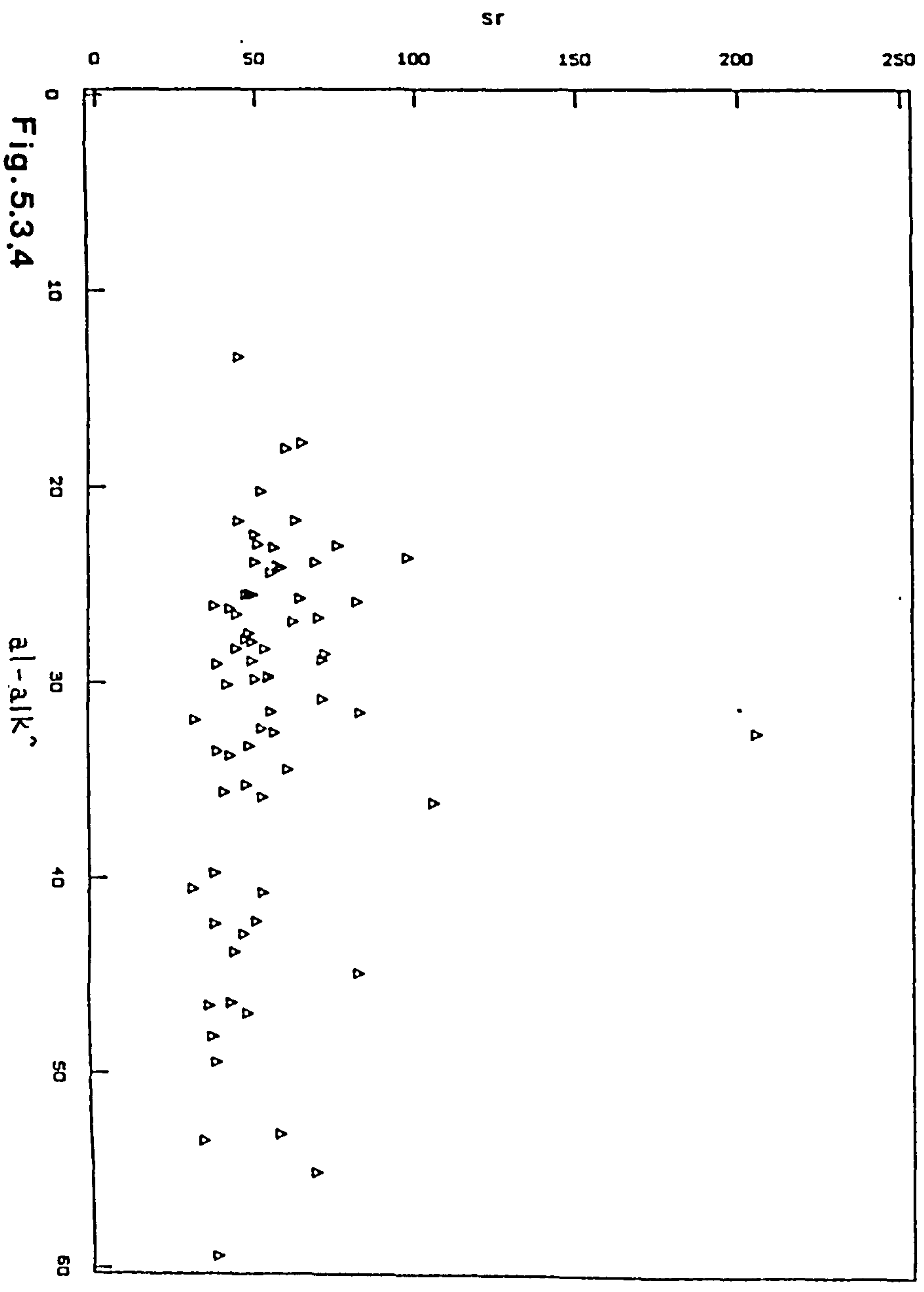


Fig. 5.3.4

Fig. 5.3.3 and 5.3.4 Sr vs CaO and al-alk

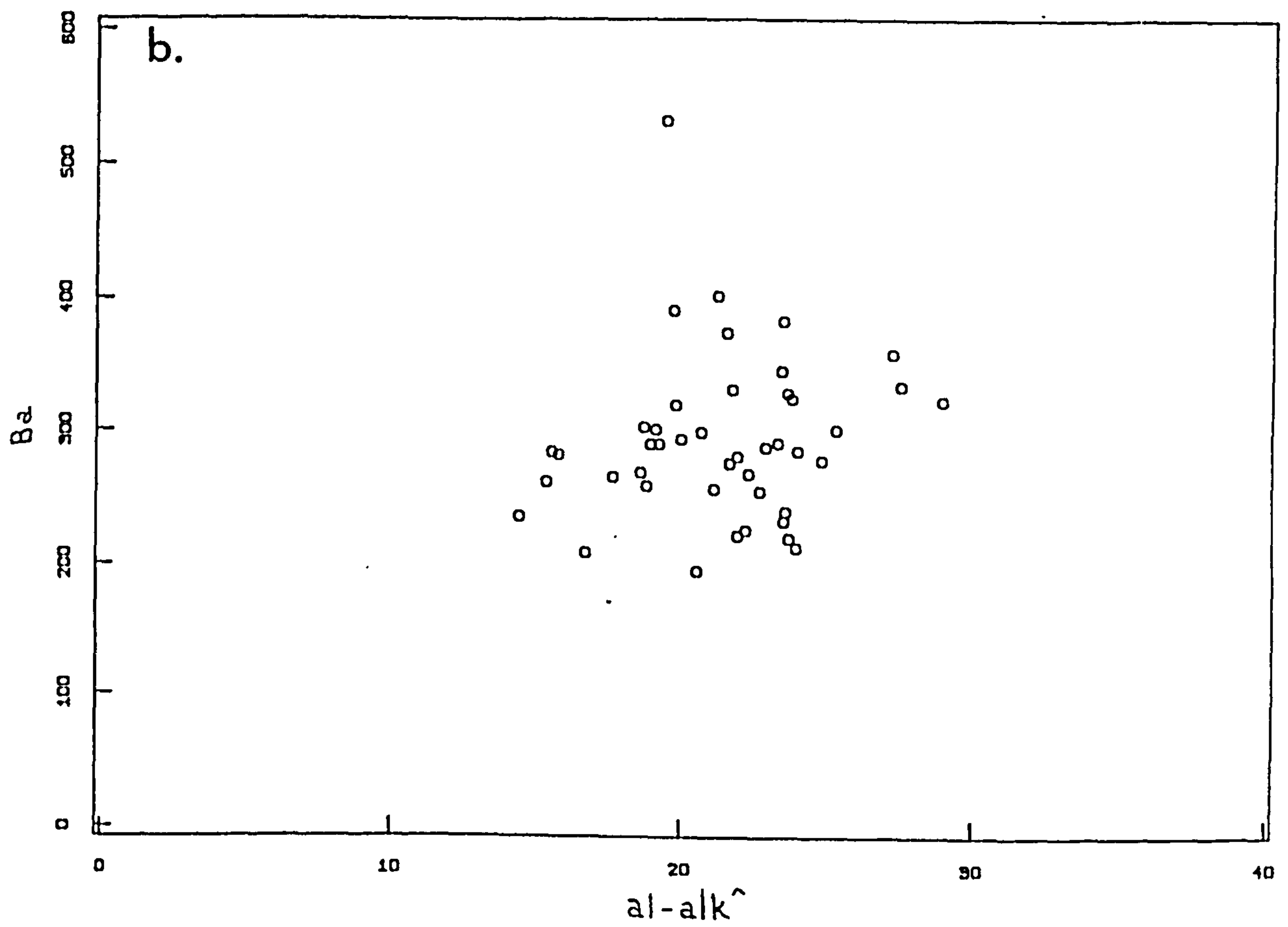
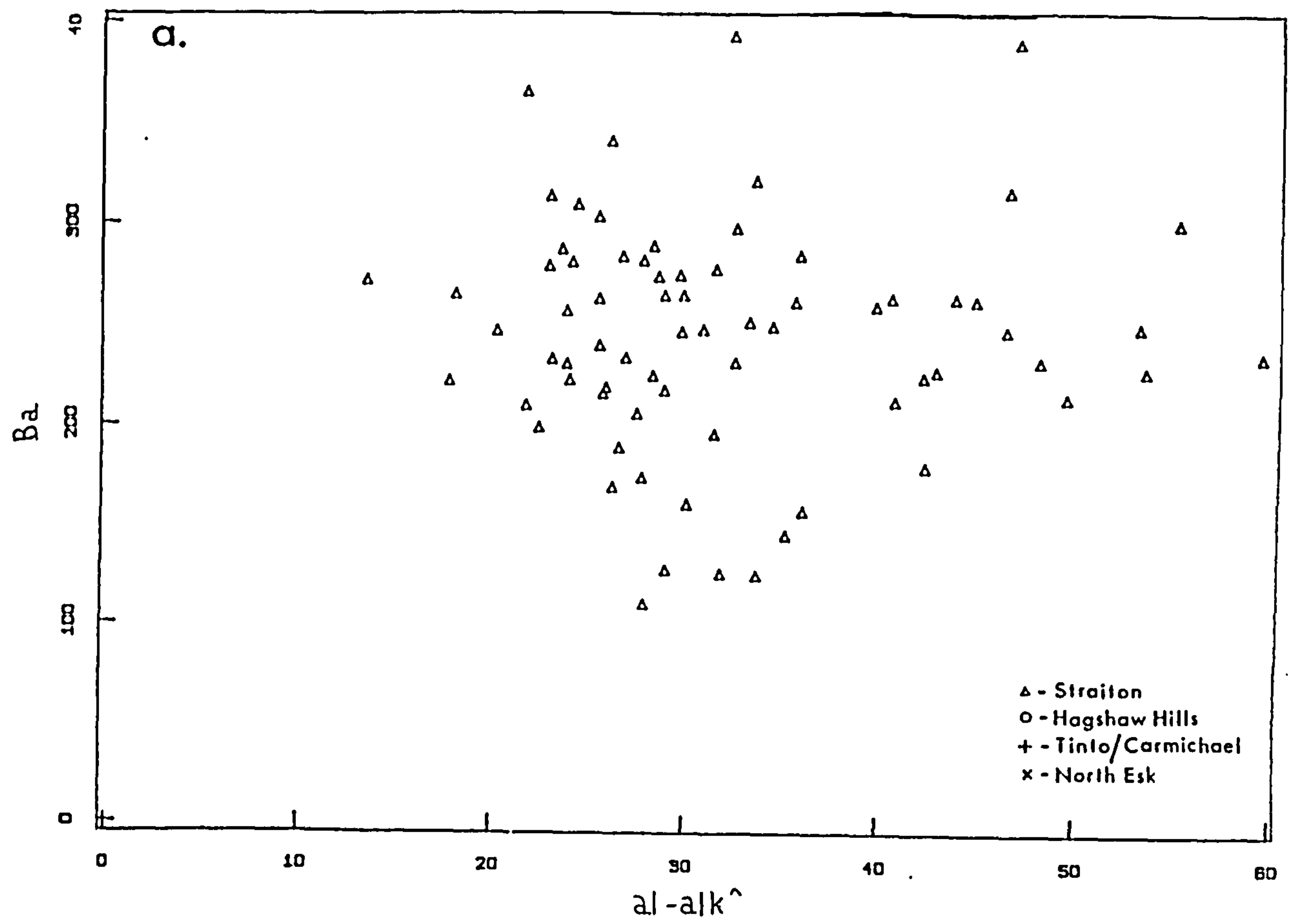


Fig. 5.3.5 (a-b) Ba vs $al-alk^+$

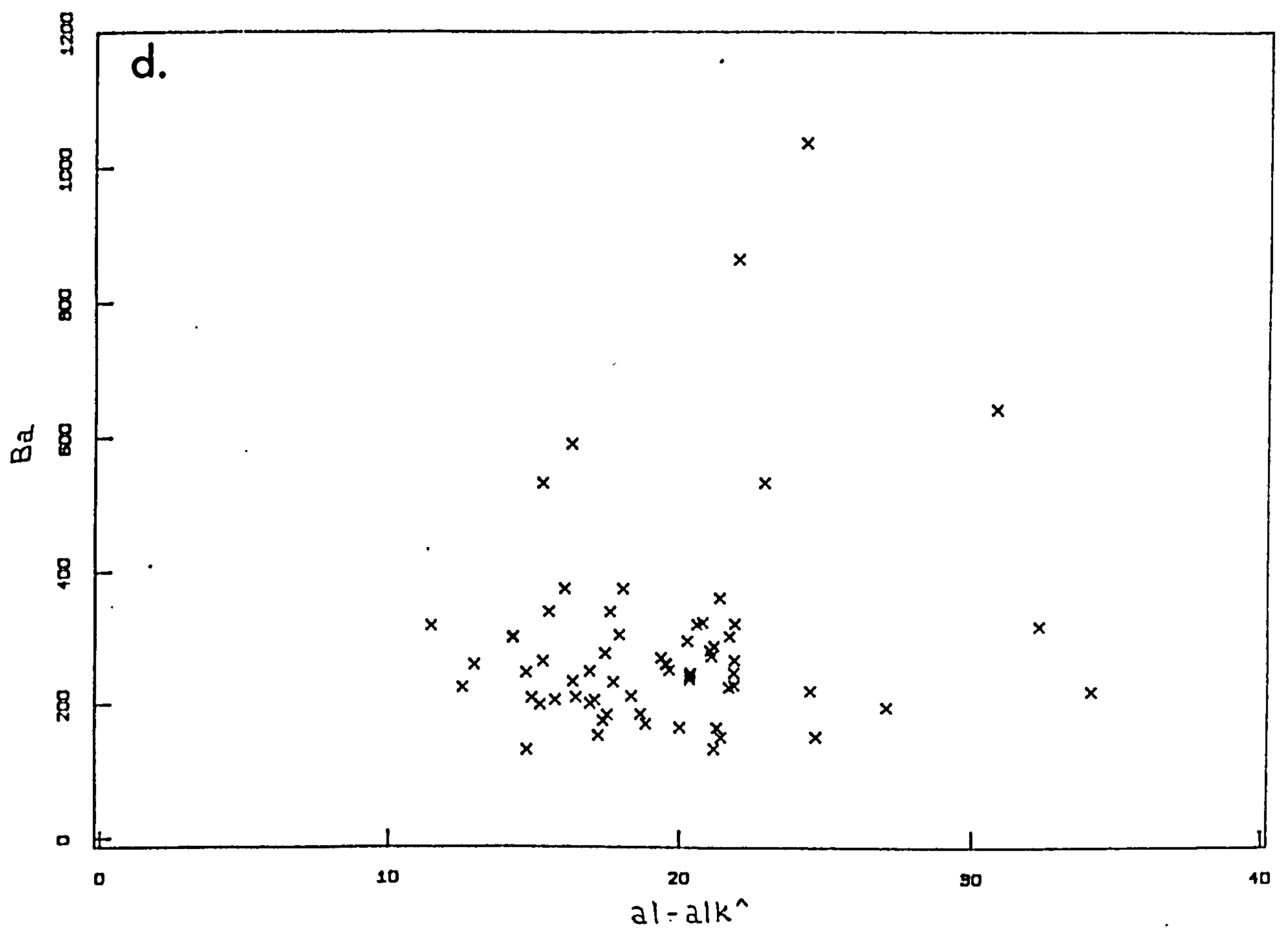
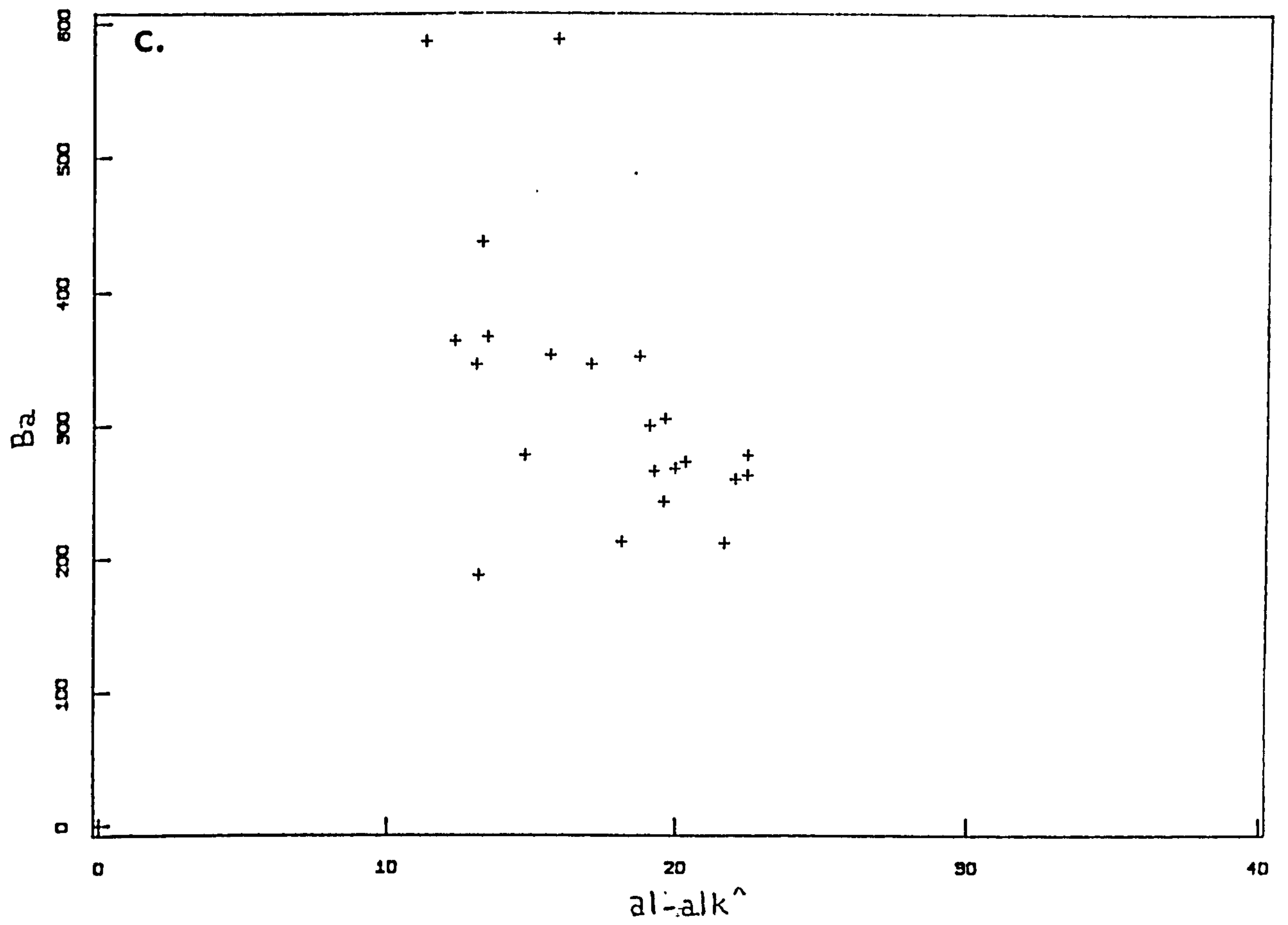


Fig. 5.3.5 (c-d) Ba vs al⁺-alk⁺

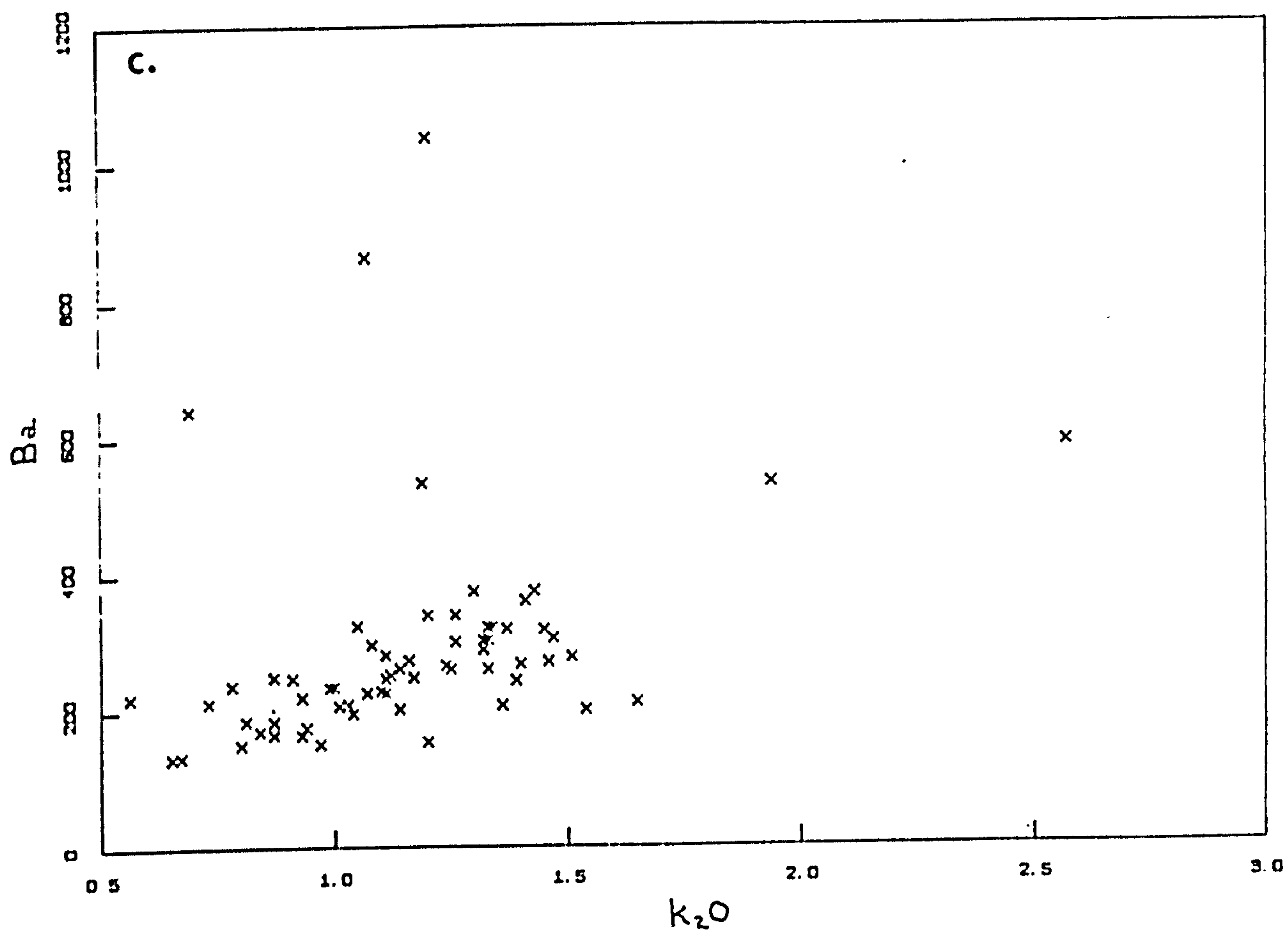


Fig. 5.3.6 (c) Ba vs k_2O

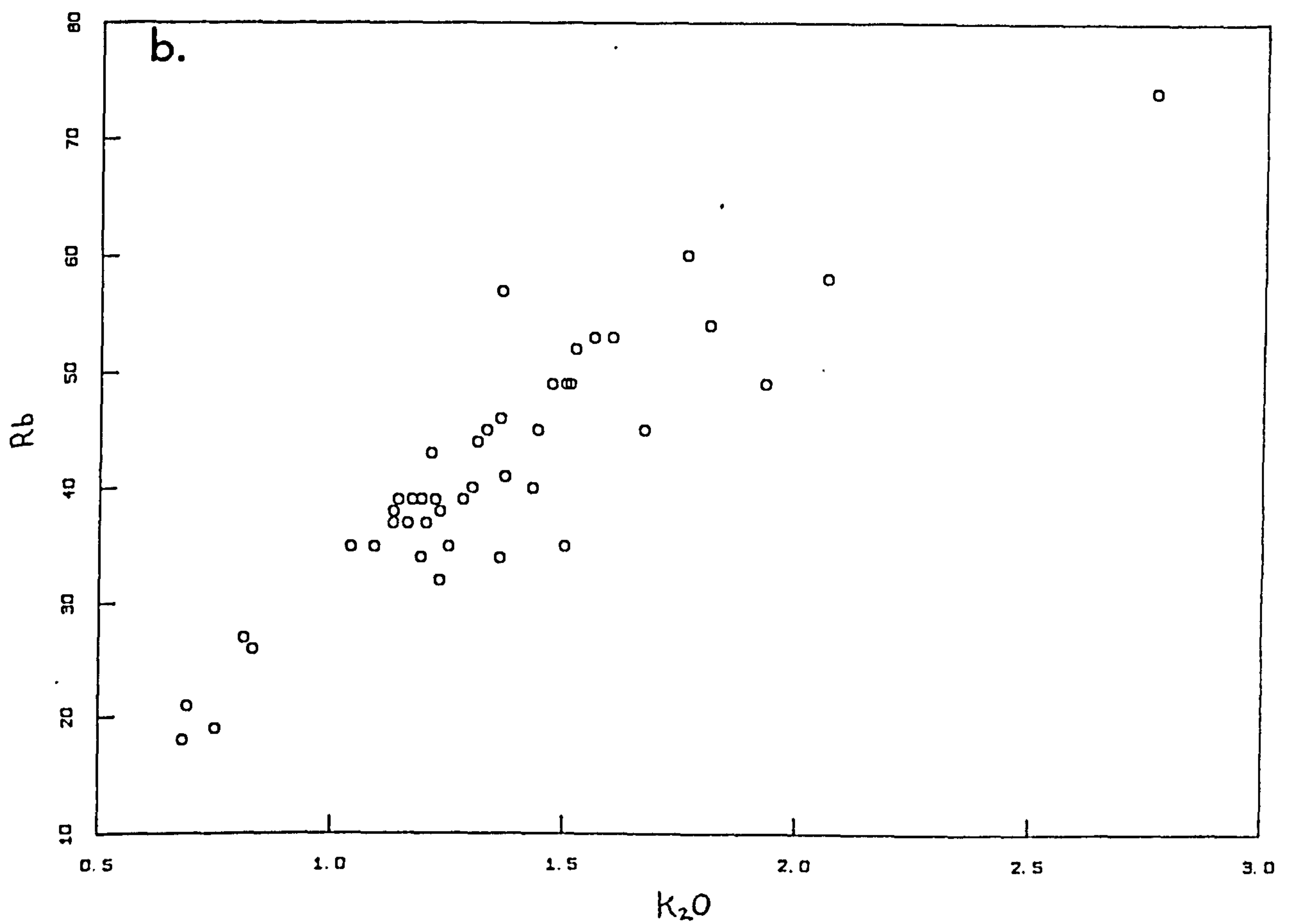
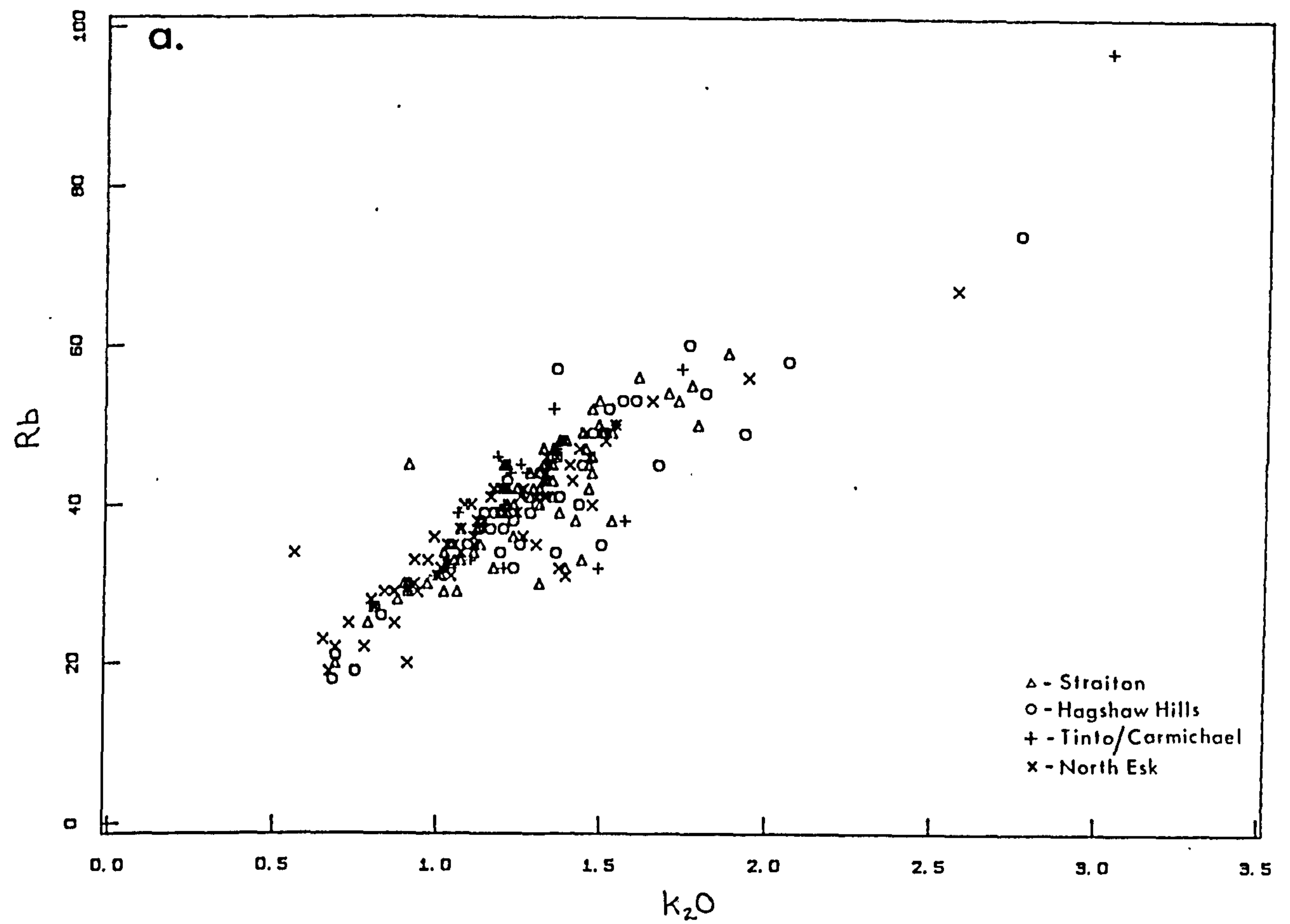


Fig. 5.3.7 (a-b) rb vs k_2O

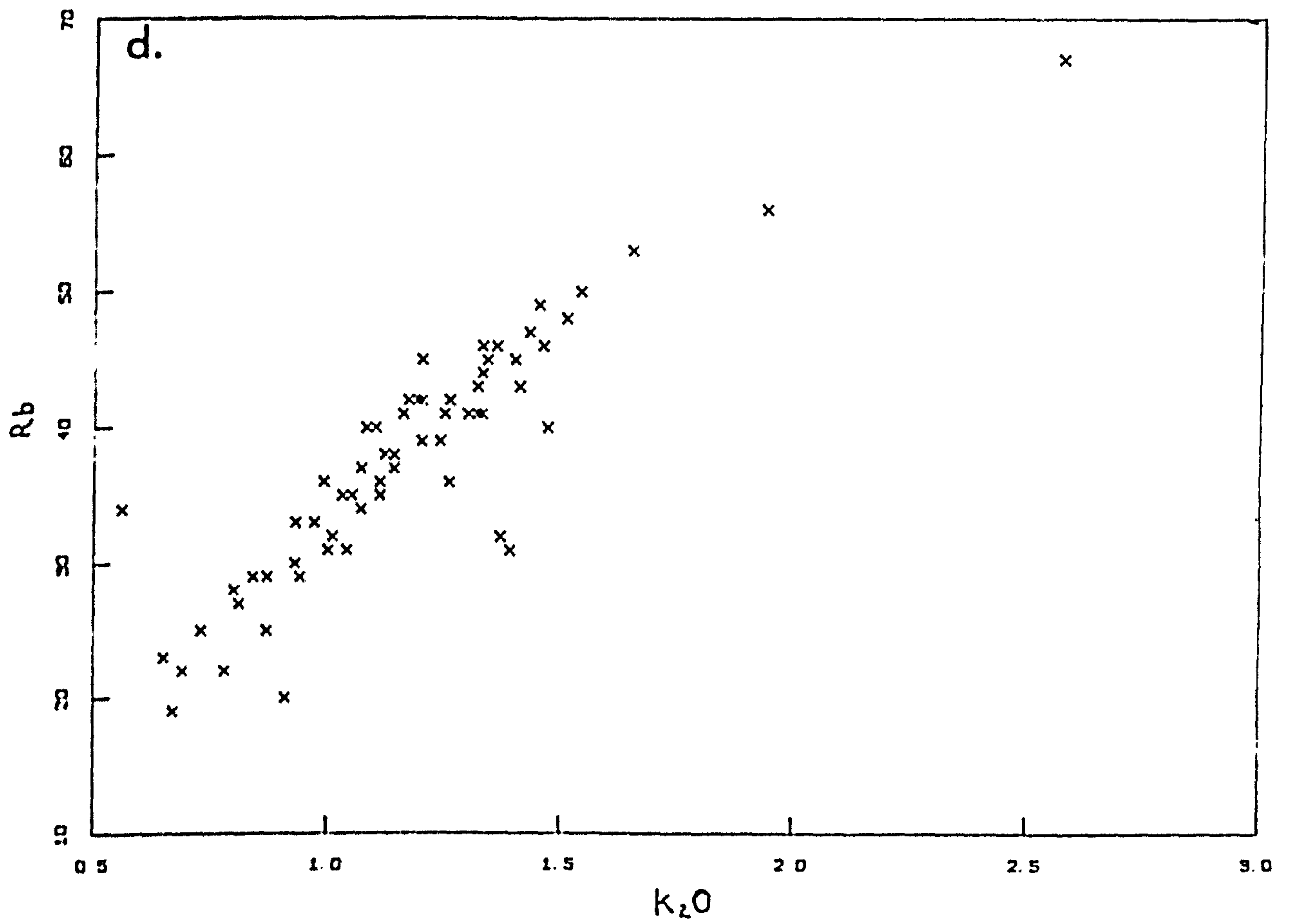
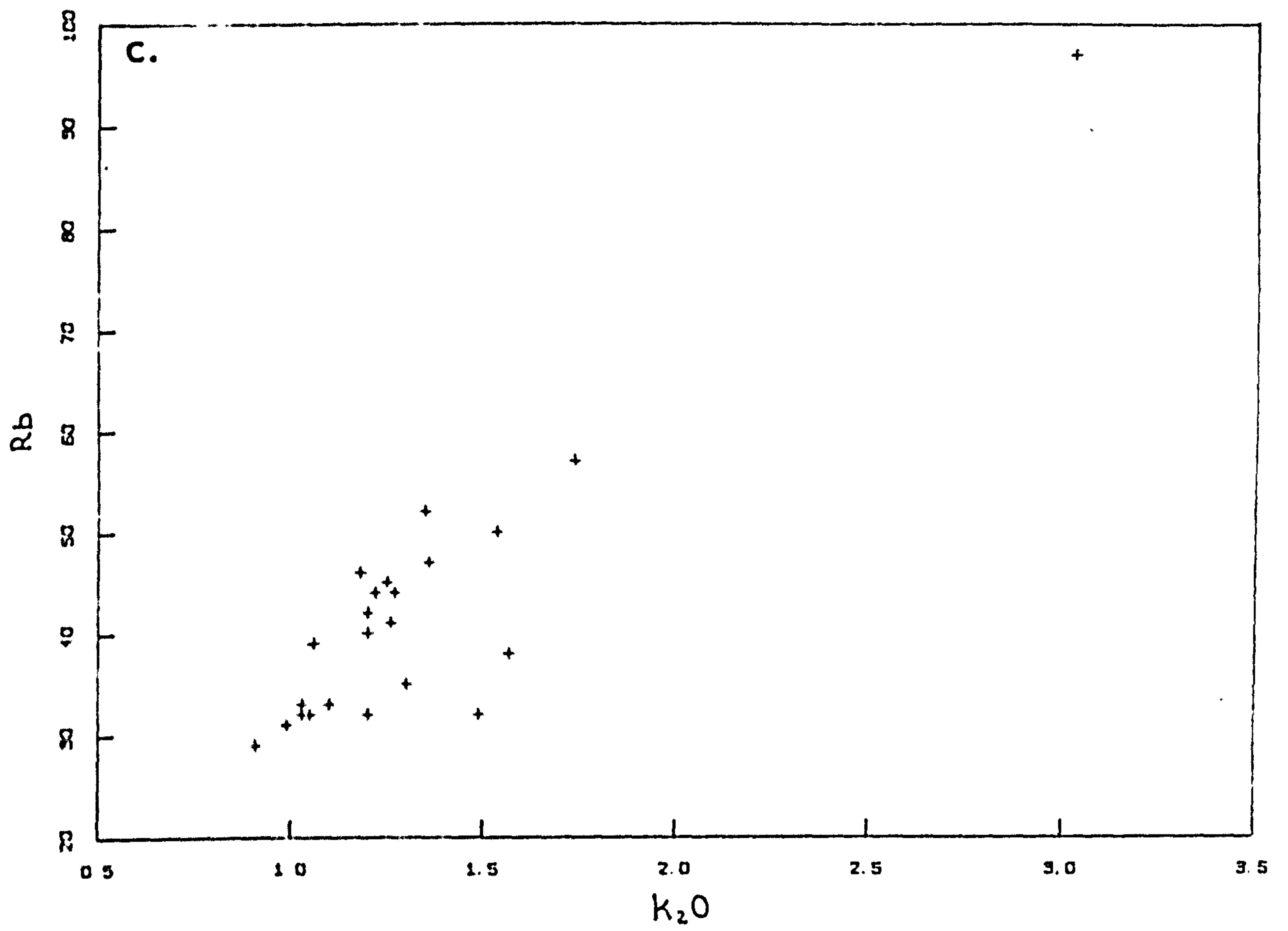


Fig. 5.3.7 (c-d) rb vs k_2O

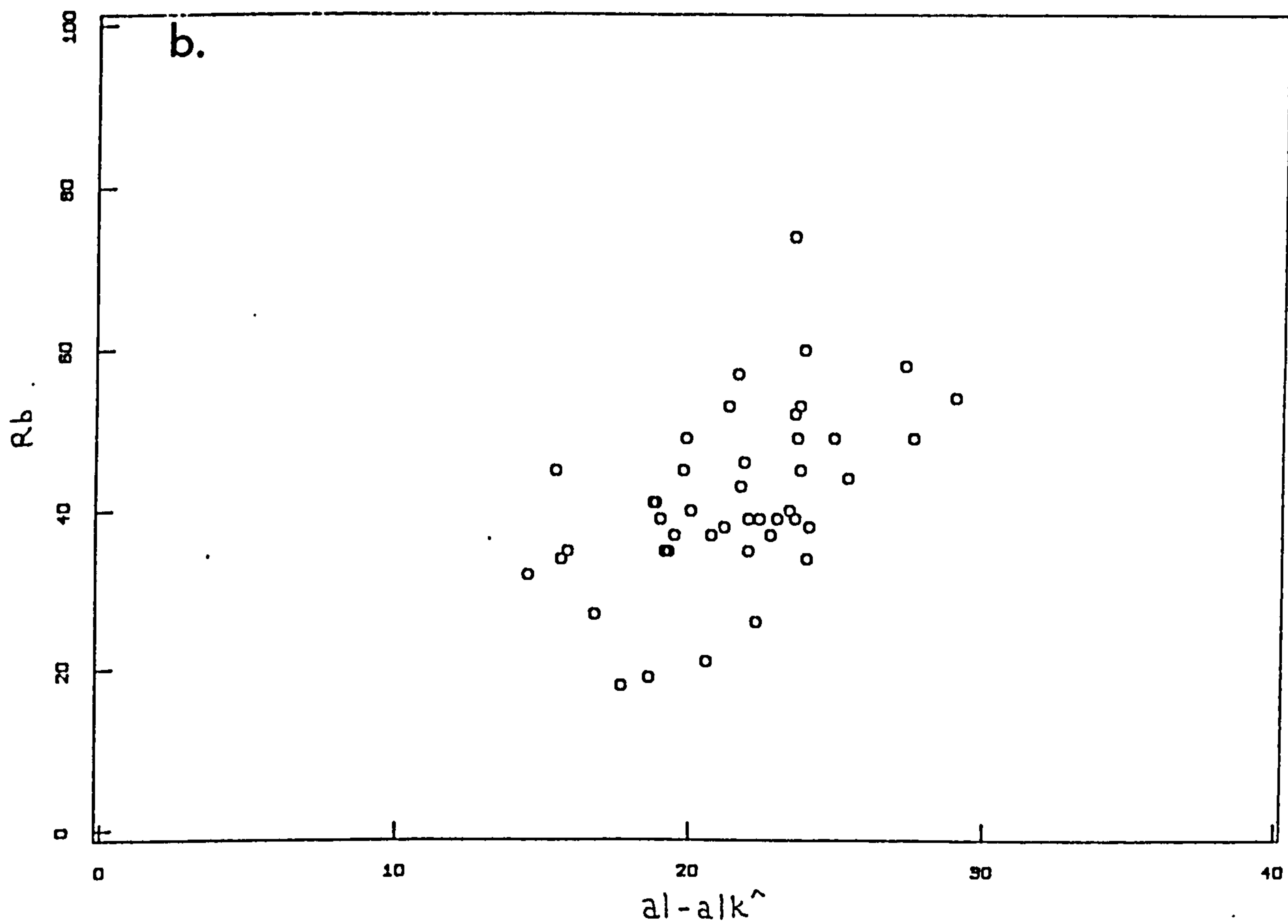
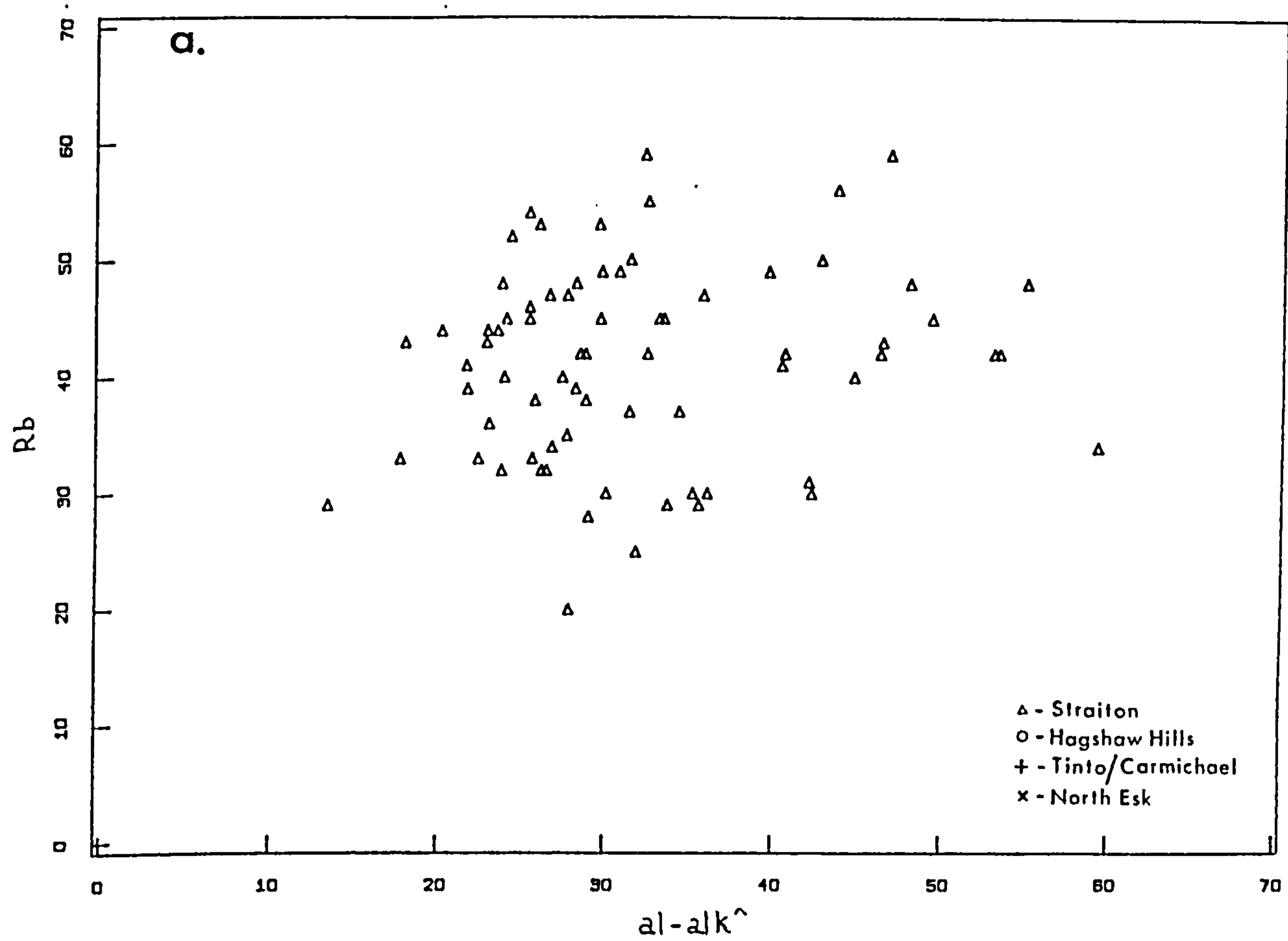


Fig. 5.3.8 (a-b) rb vs $al-alk^+$

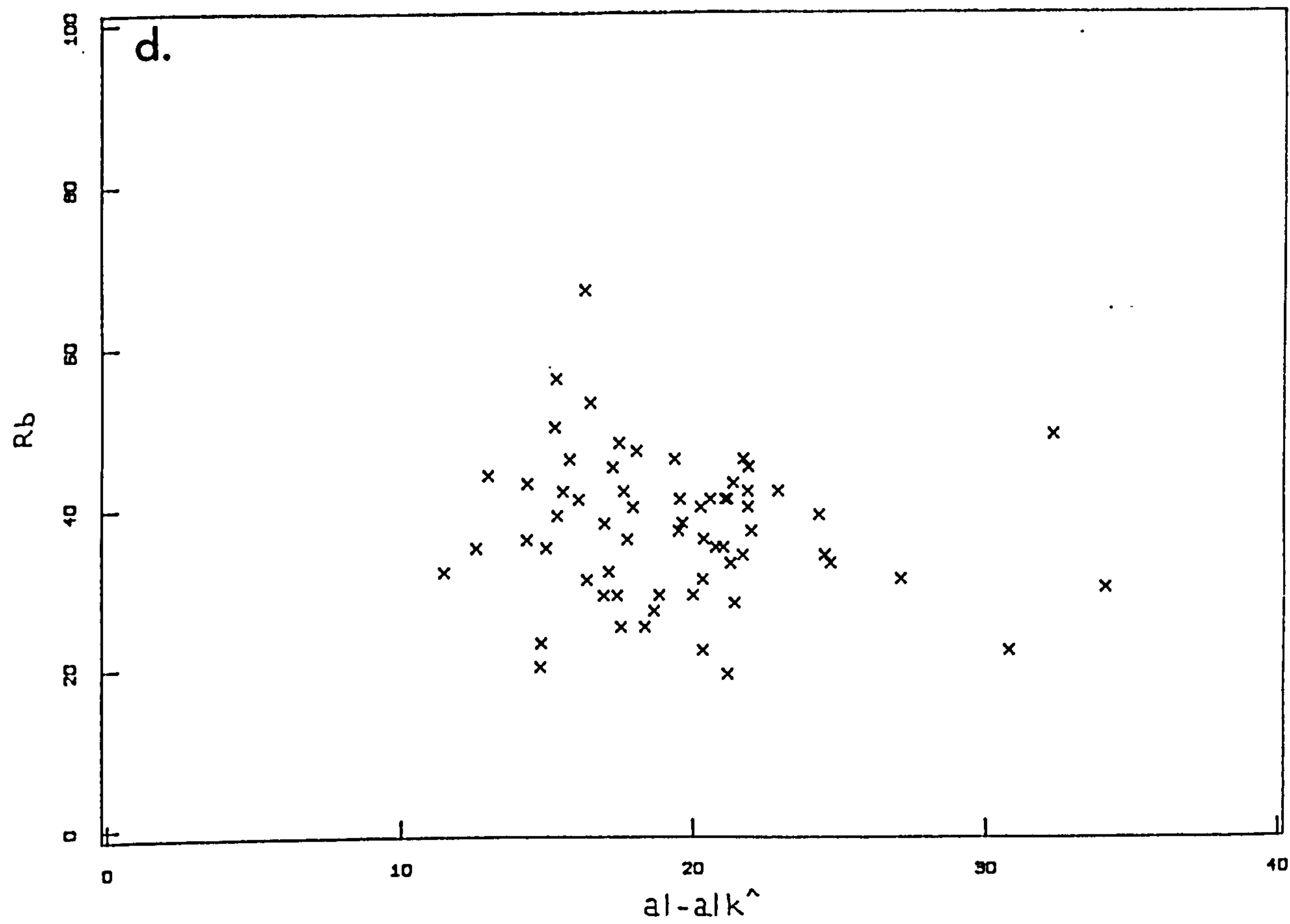
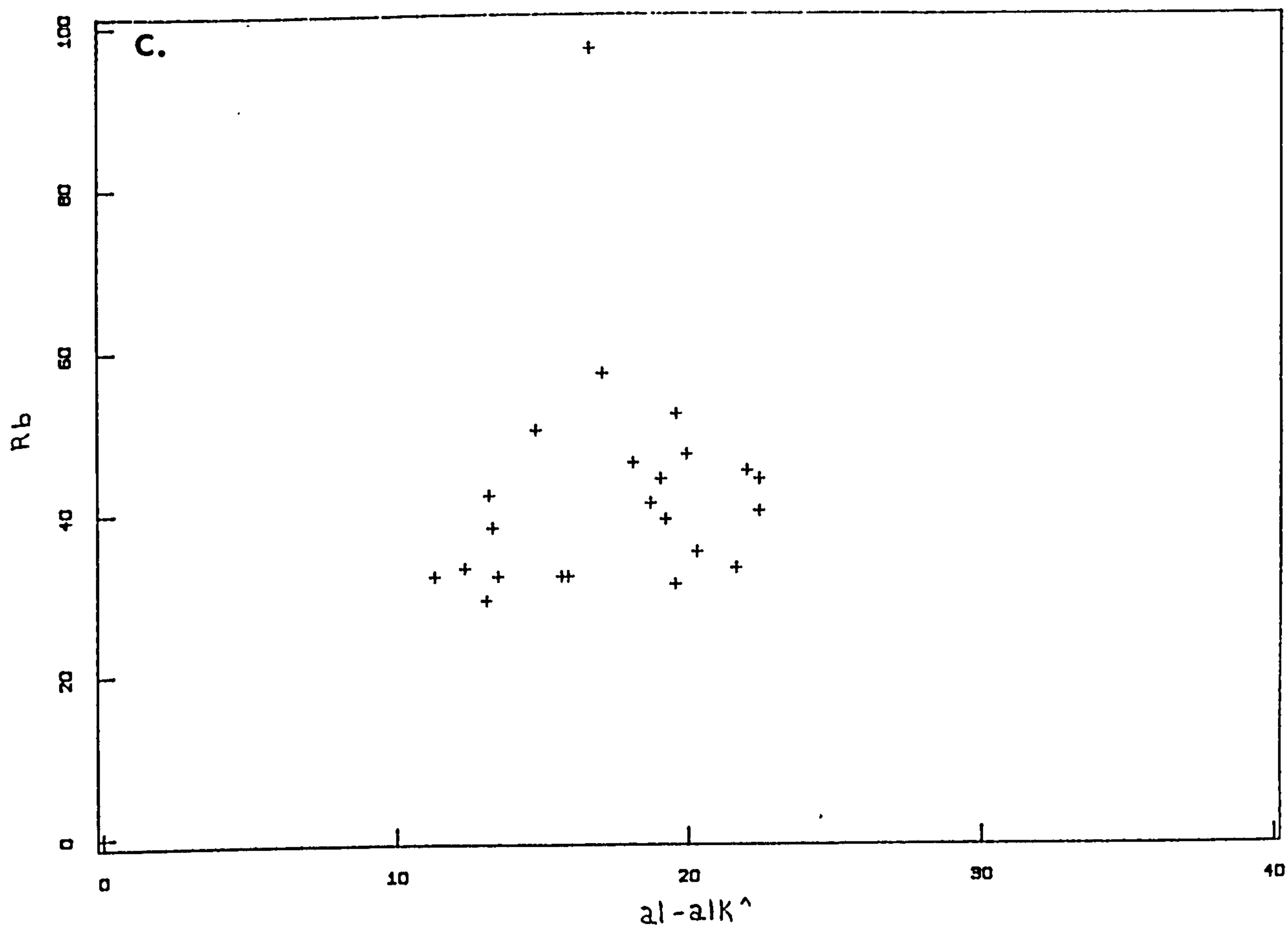


Fig. 5.3.8 (c-d) rb vs $al-alk^+$

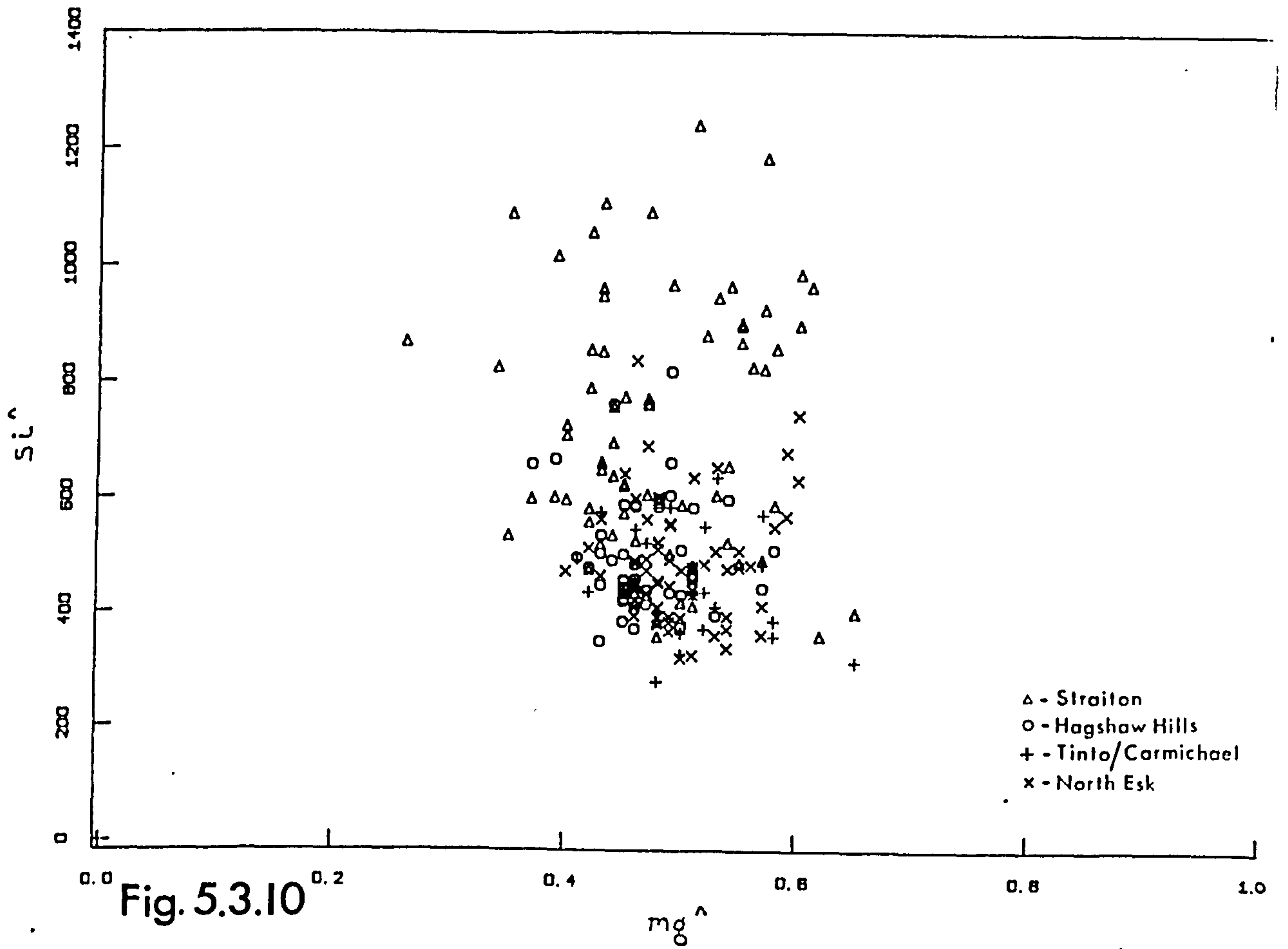
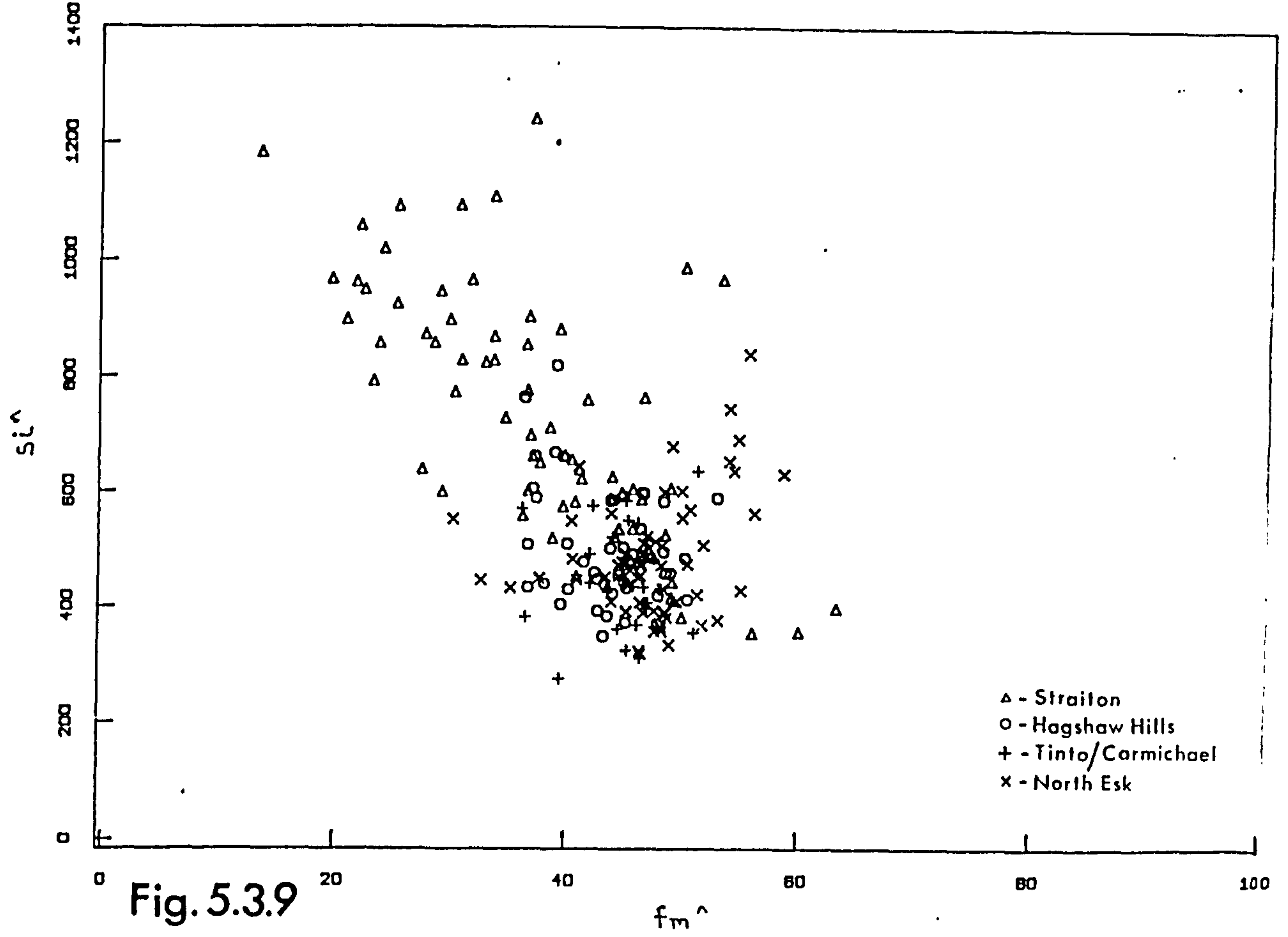


Fig. 5.3.9 and 5.3.10 $Si^$ vs $fm^$ & $mg^$

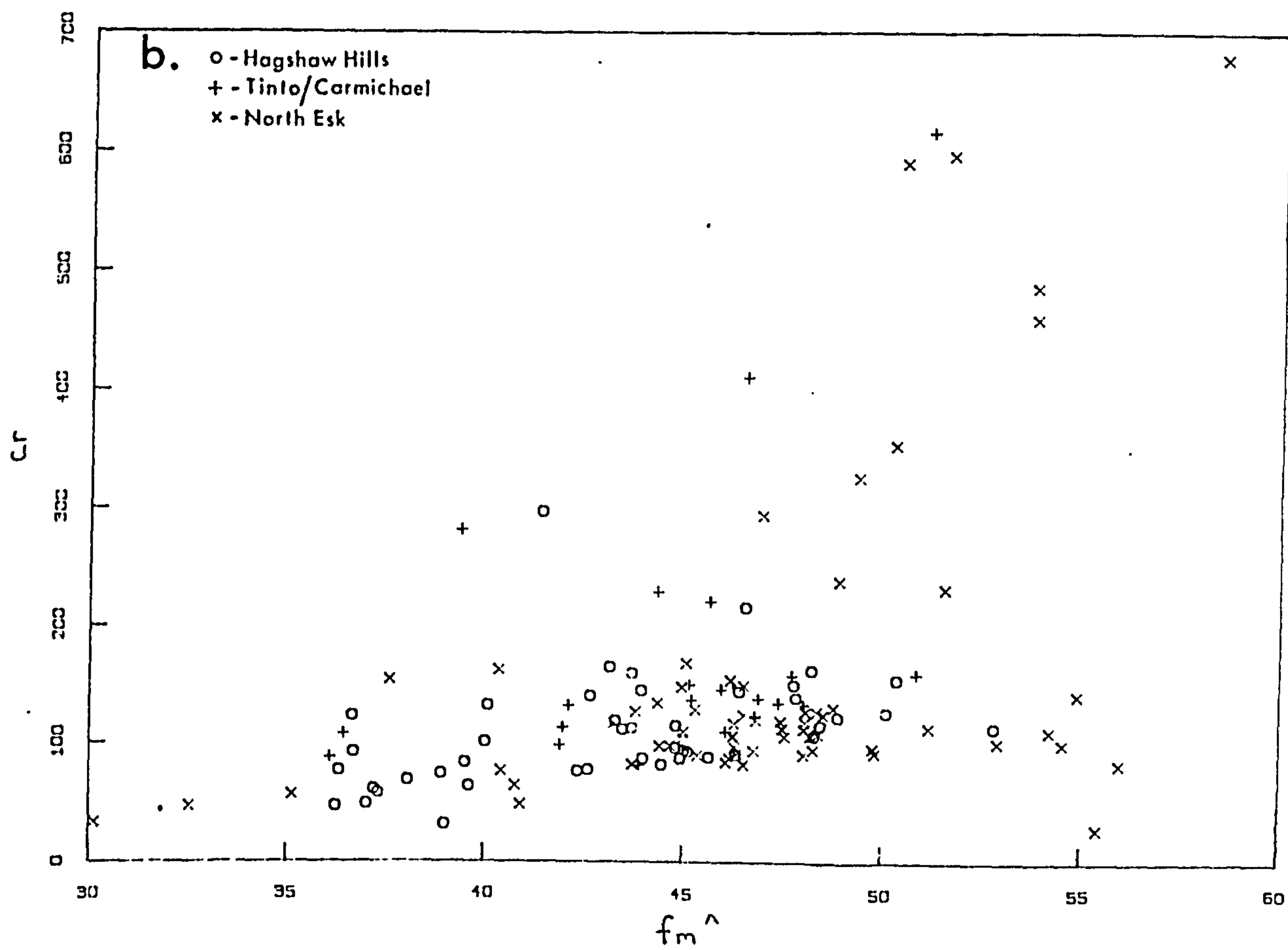
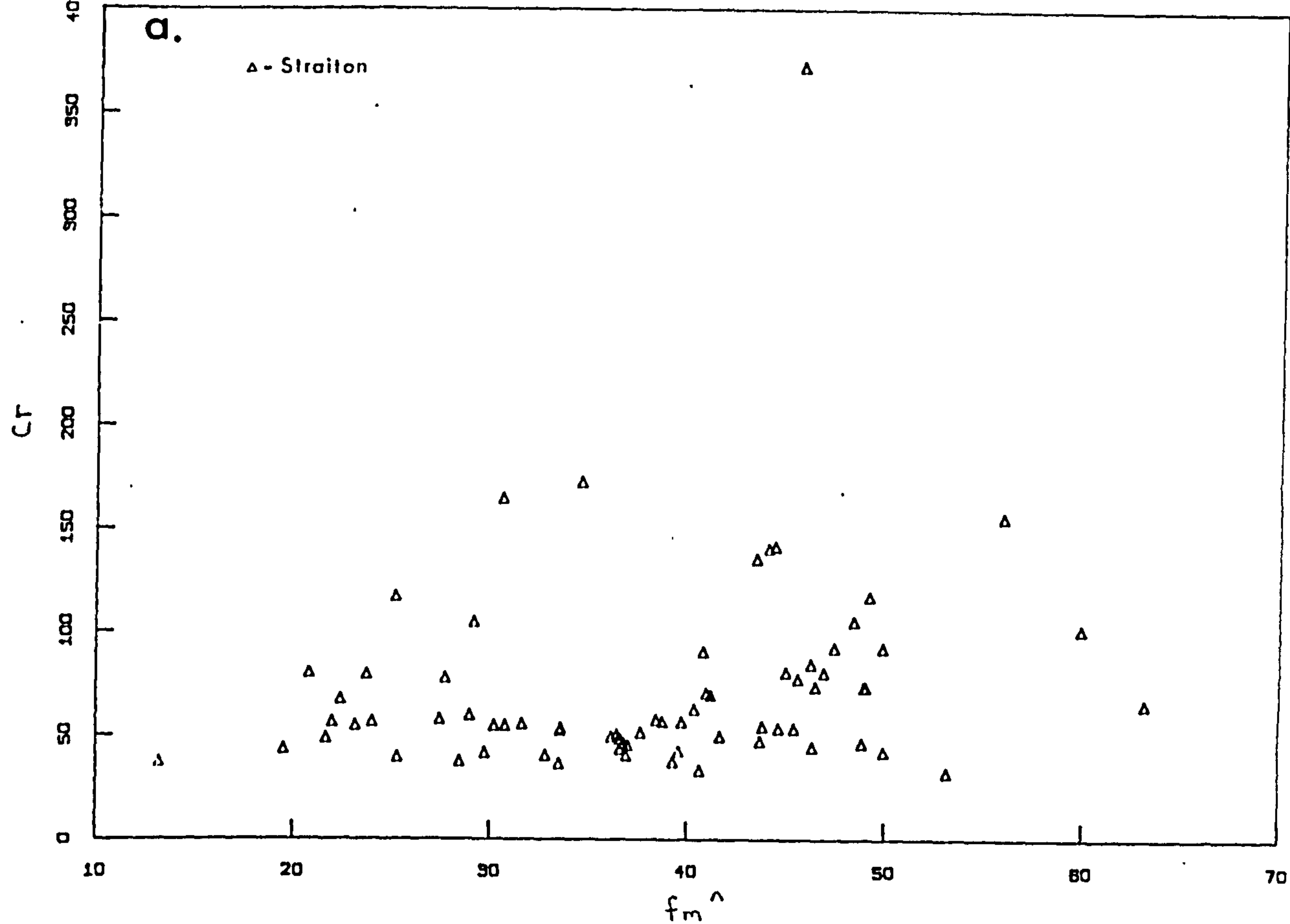


Fig. 5.3.11 (a-b) cr vs $f_m^$

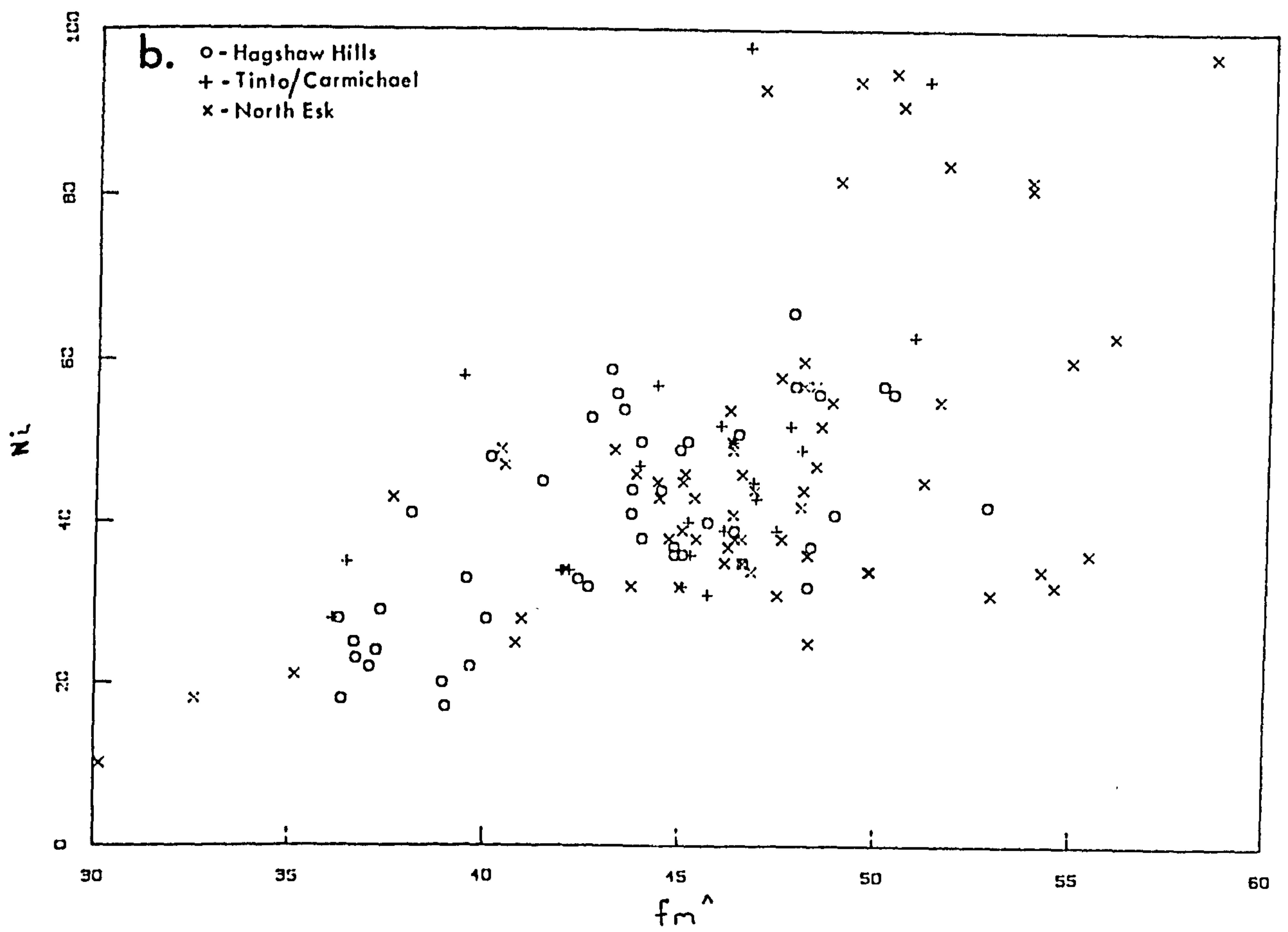
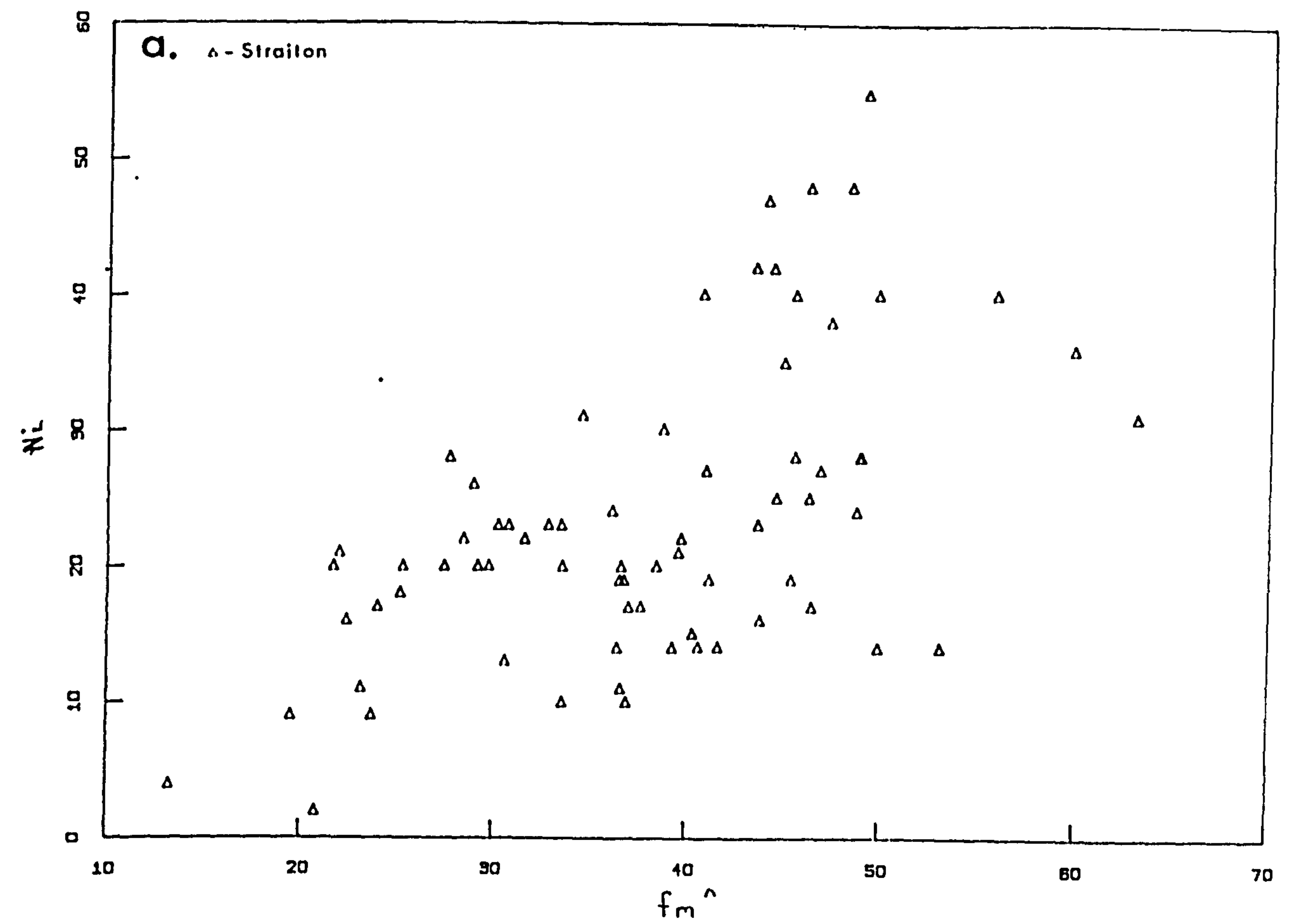


Fig. 5.3.12 (a-b) ni vs $fm^$

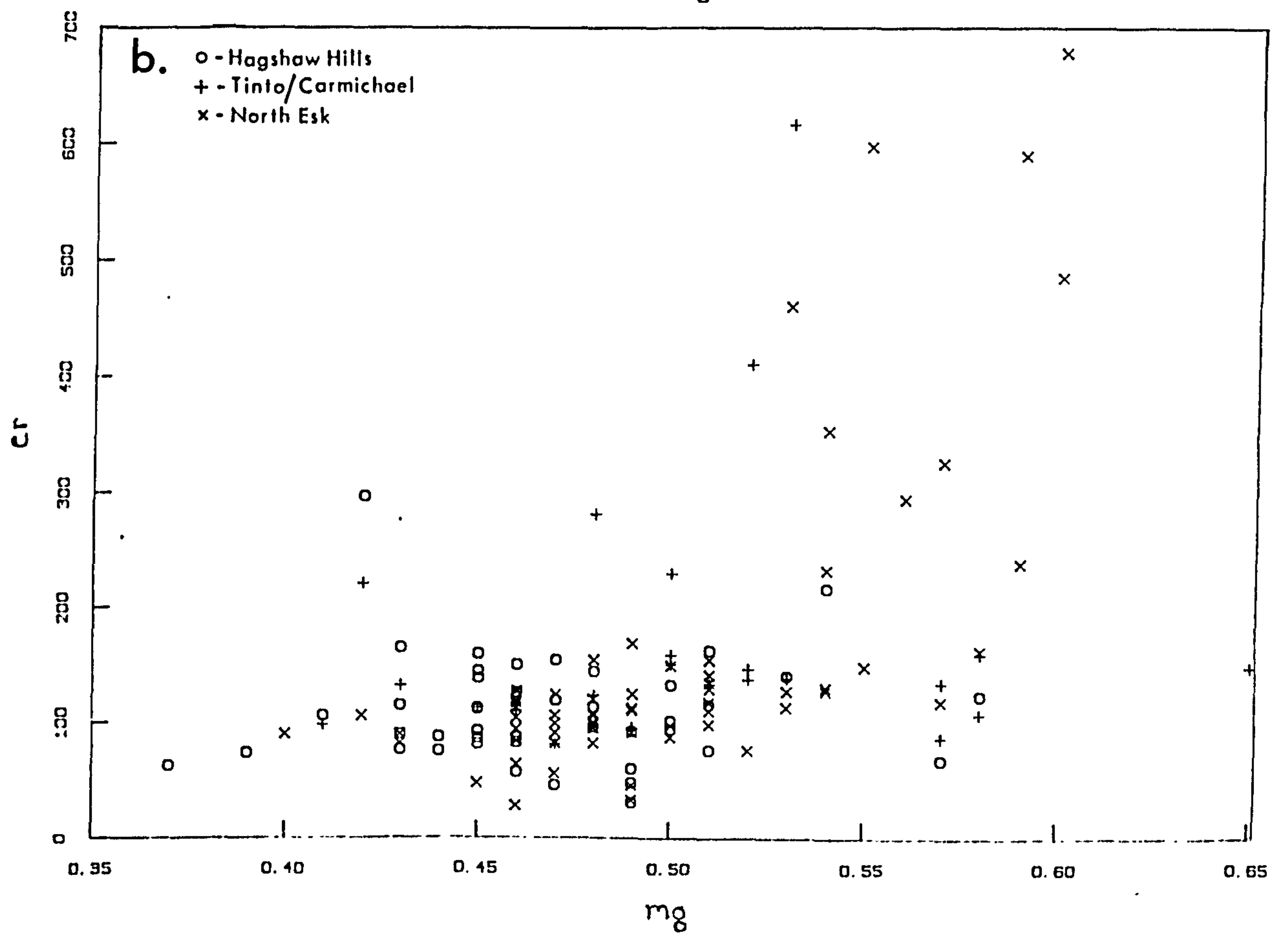
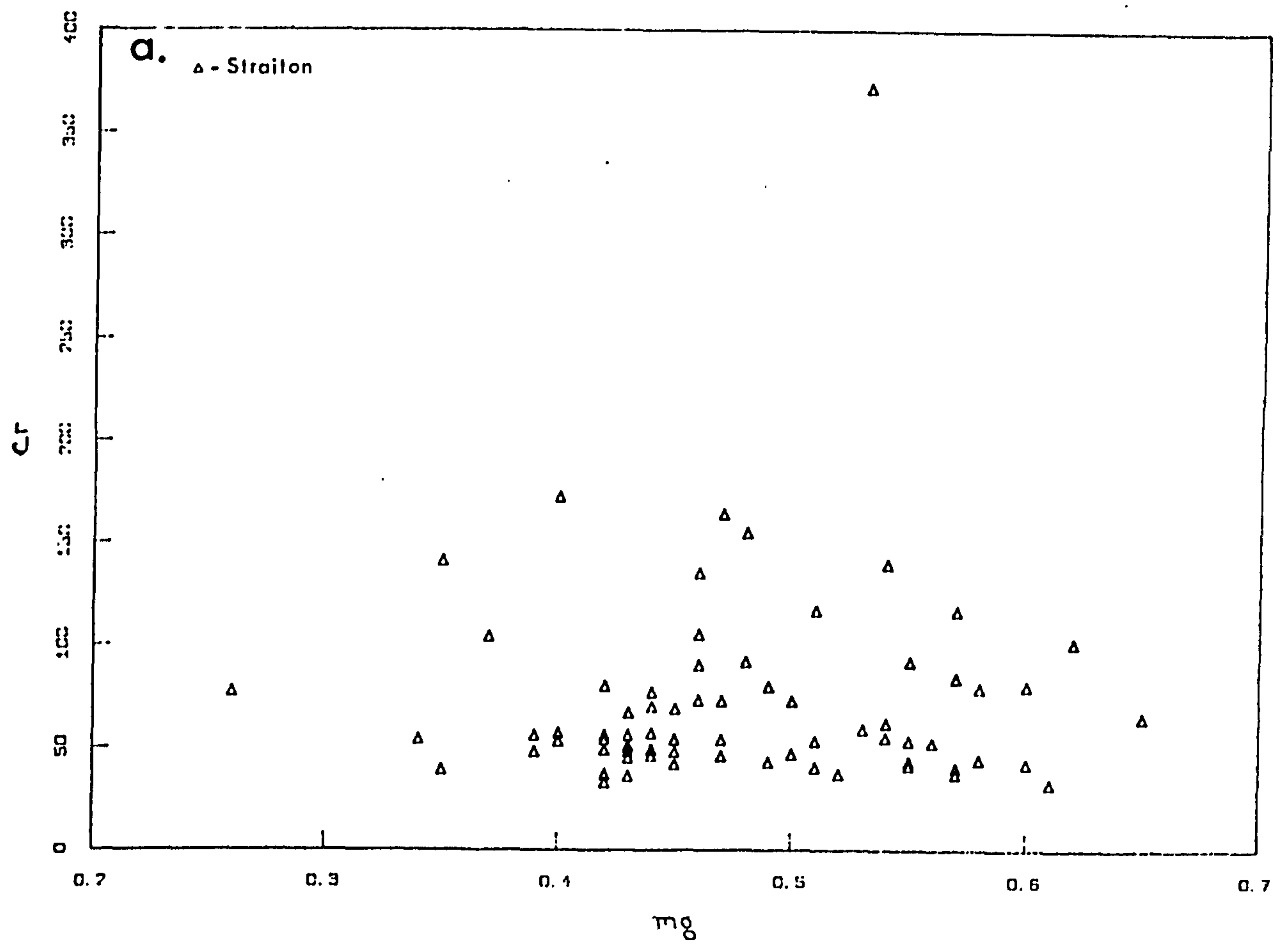


Fig. 5.3.13 (a-b) cr vs mg[^]

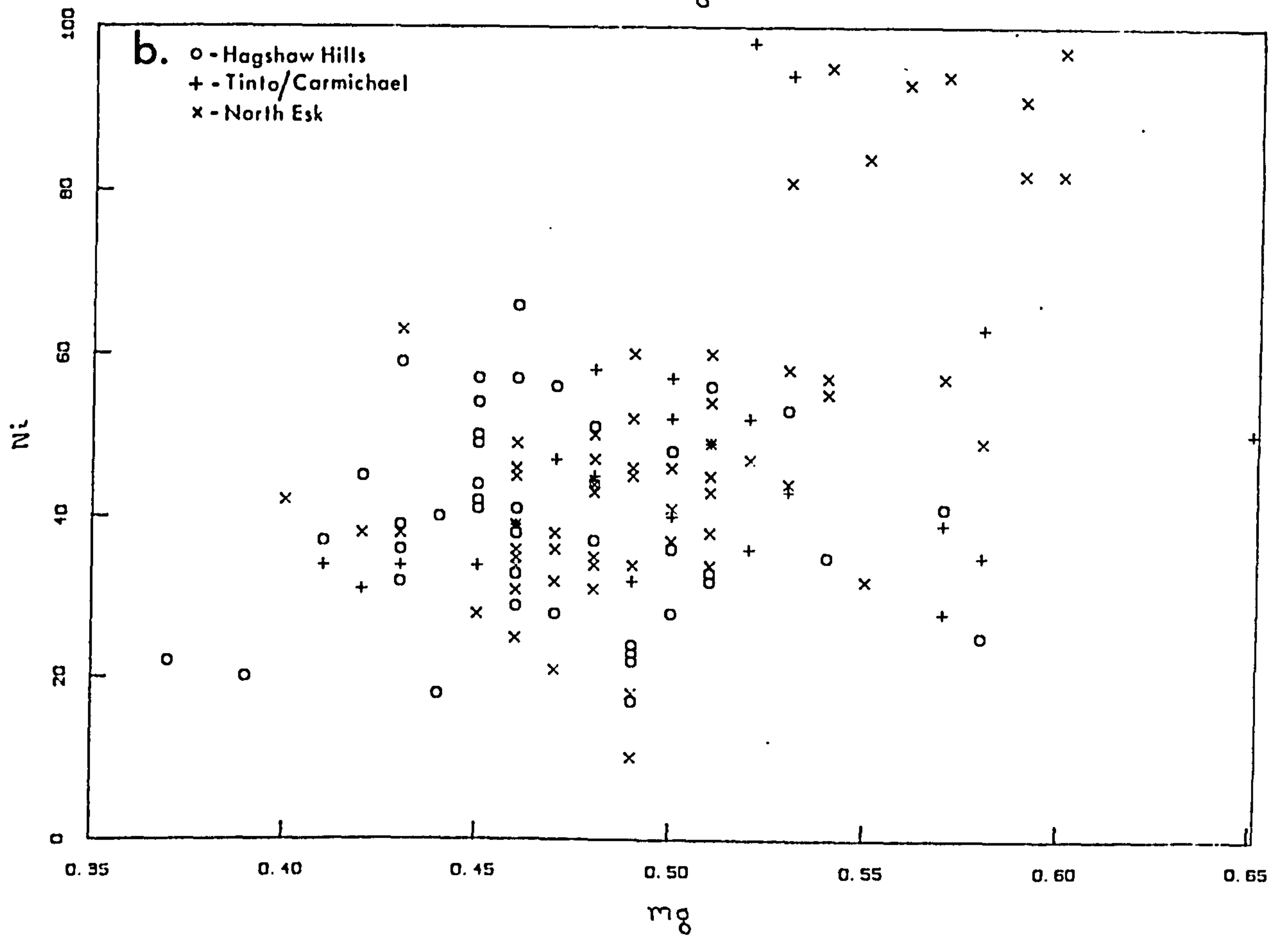
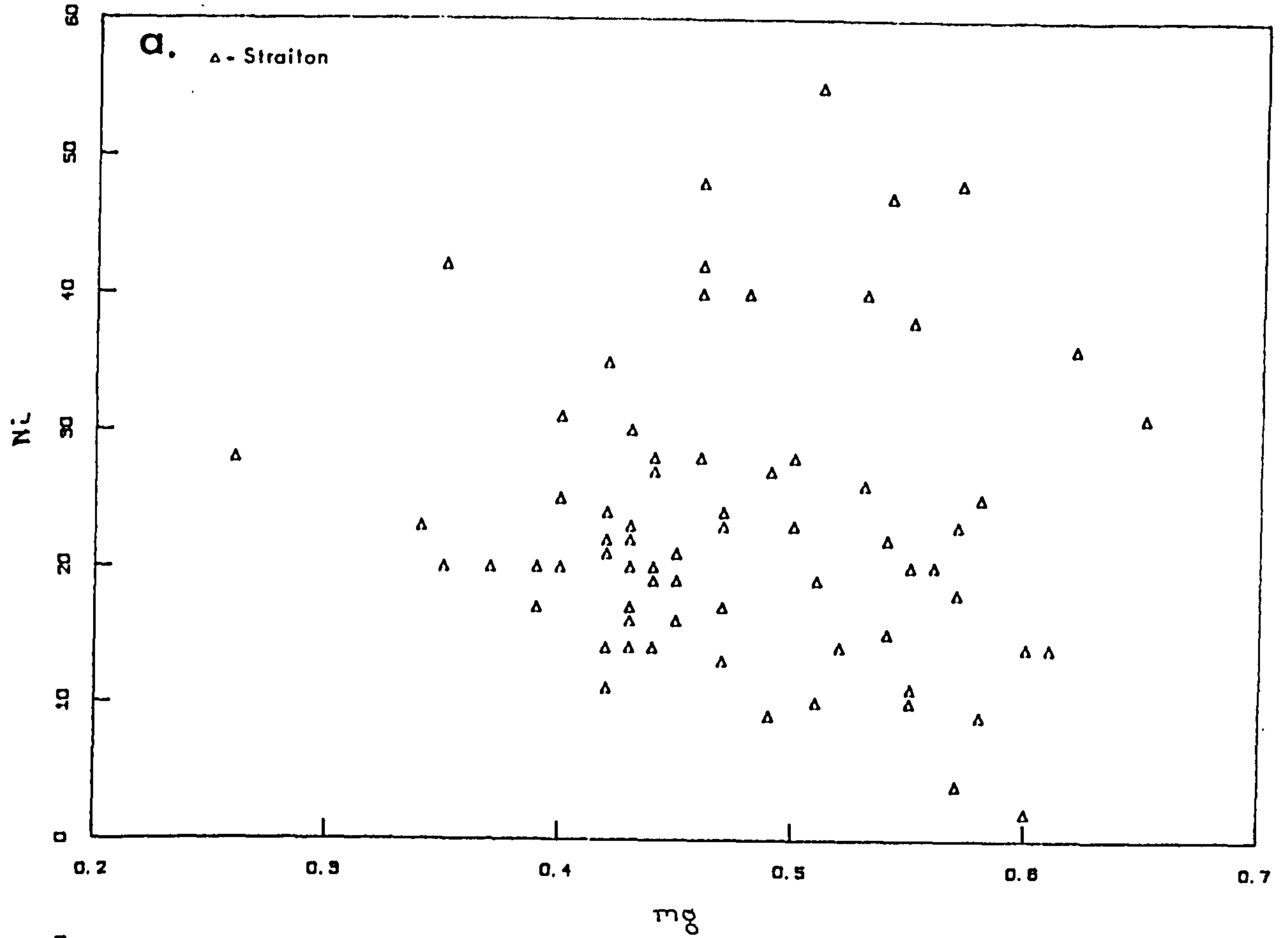


Fig. 5.3.14 (a-b) ni vs mg[^]

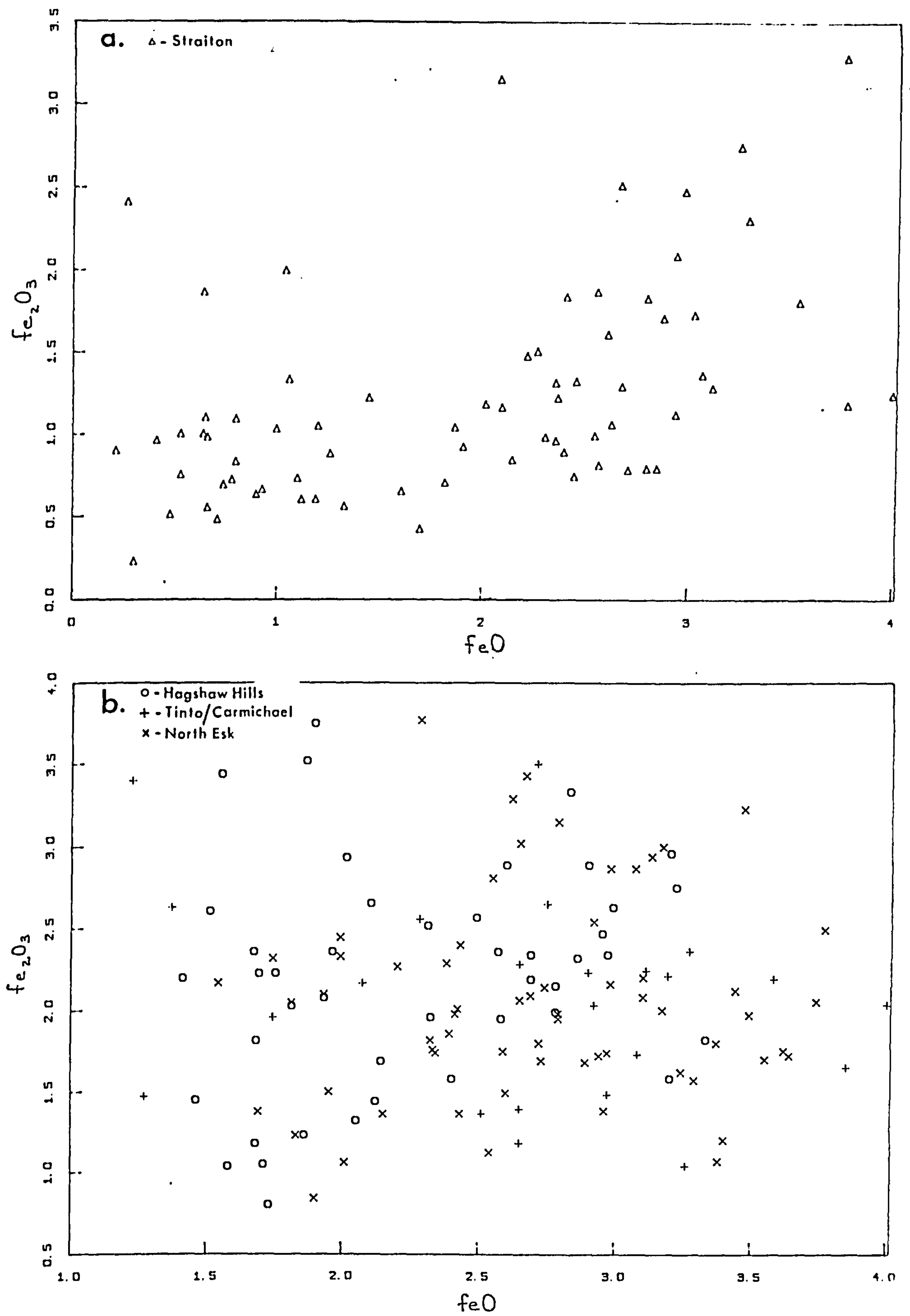


Fig. 5.3.15 (a-b) FeO vs Fe_2O_3

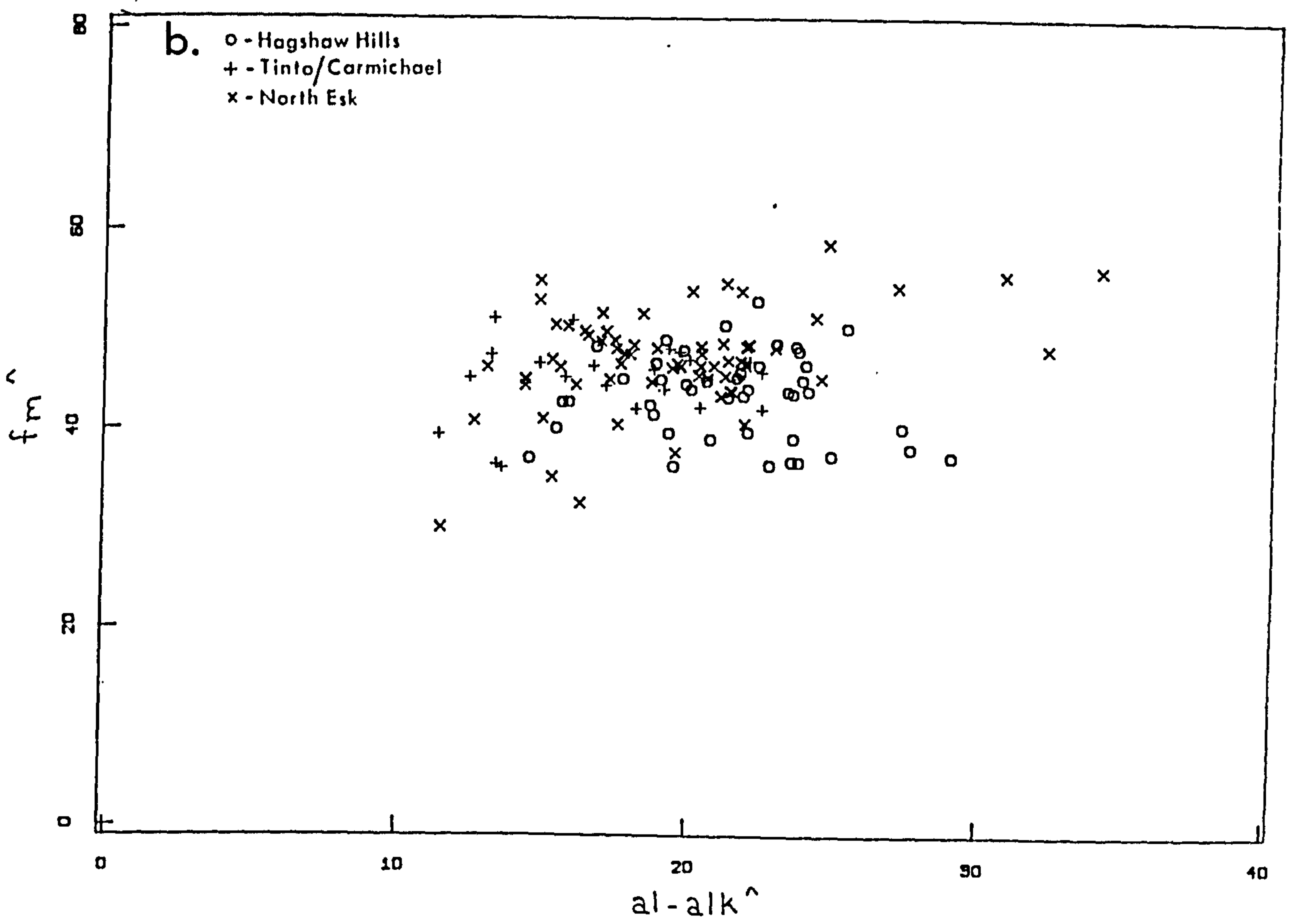
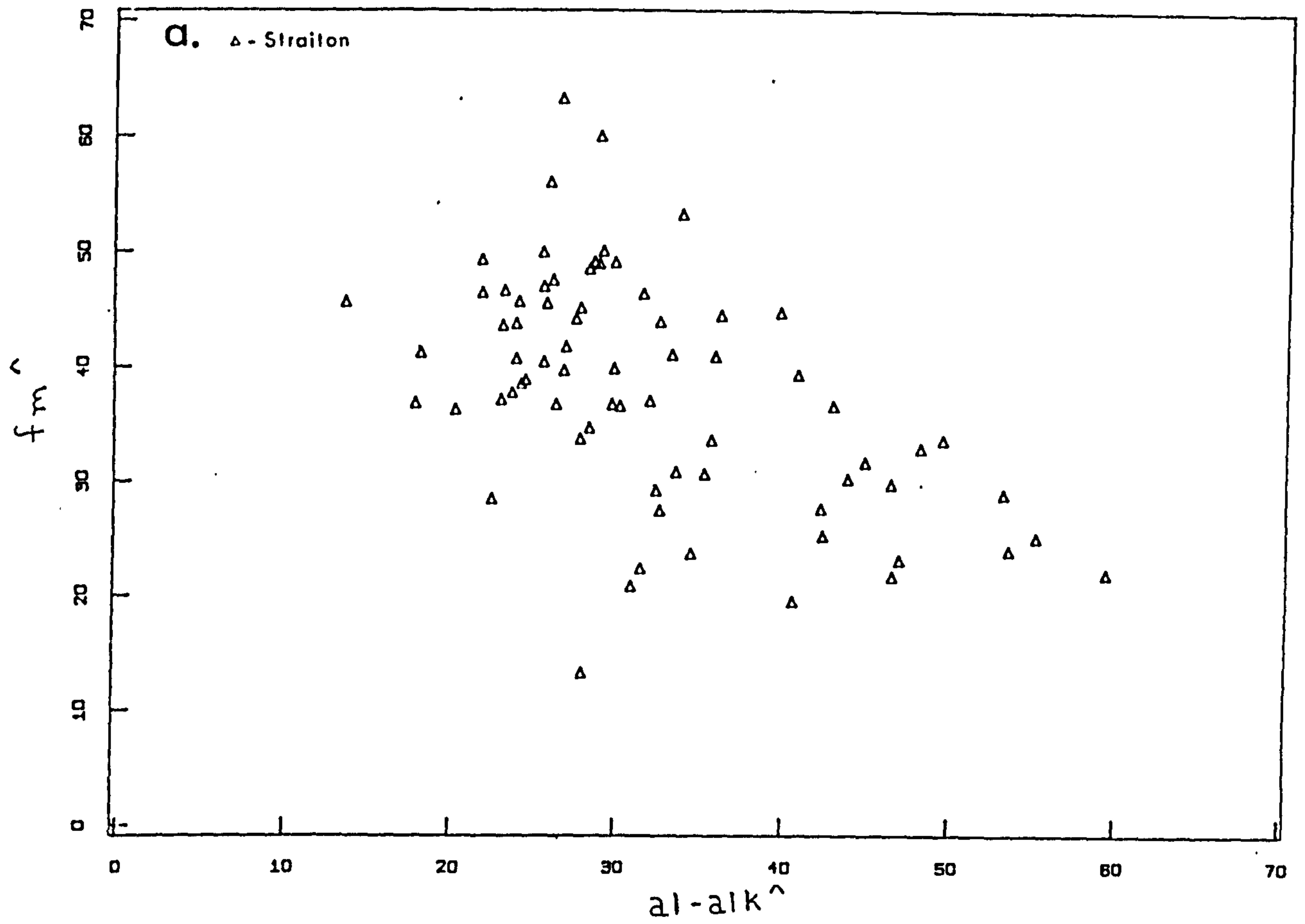


Fig. 5.3.16 (a-b) fm^2 vs $al-alk^2$

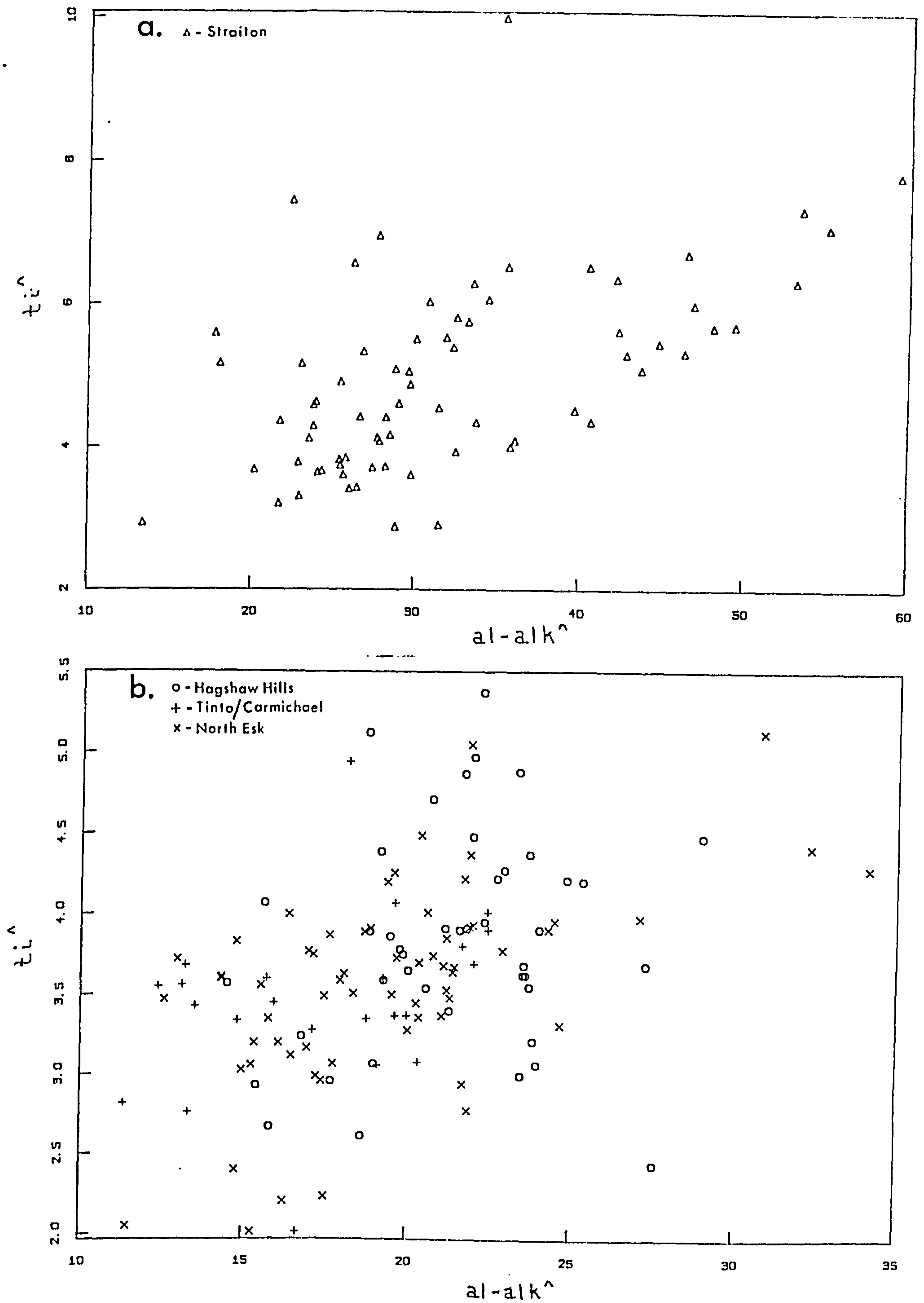


Fig. 5.3.17 (a-b) Ti^{Al} vs $Al-Alk^{Al}$

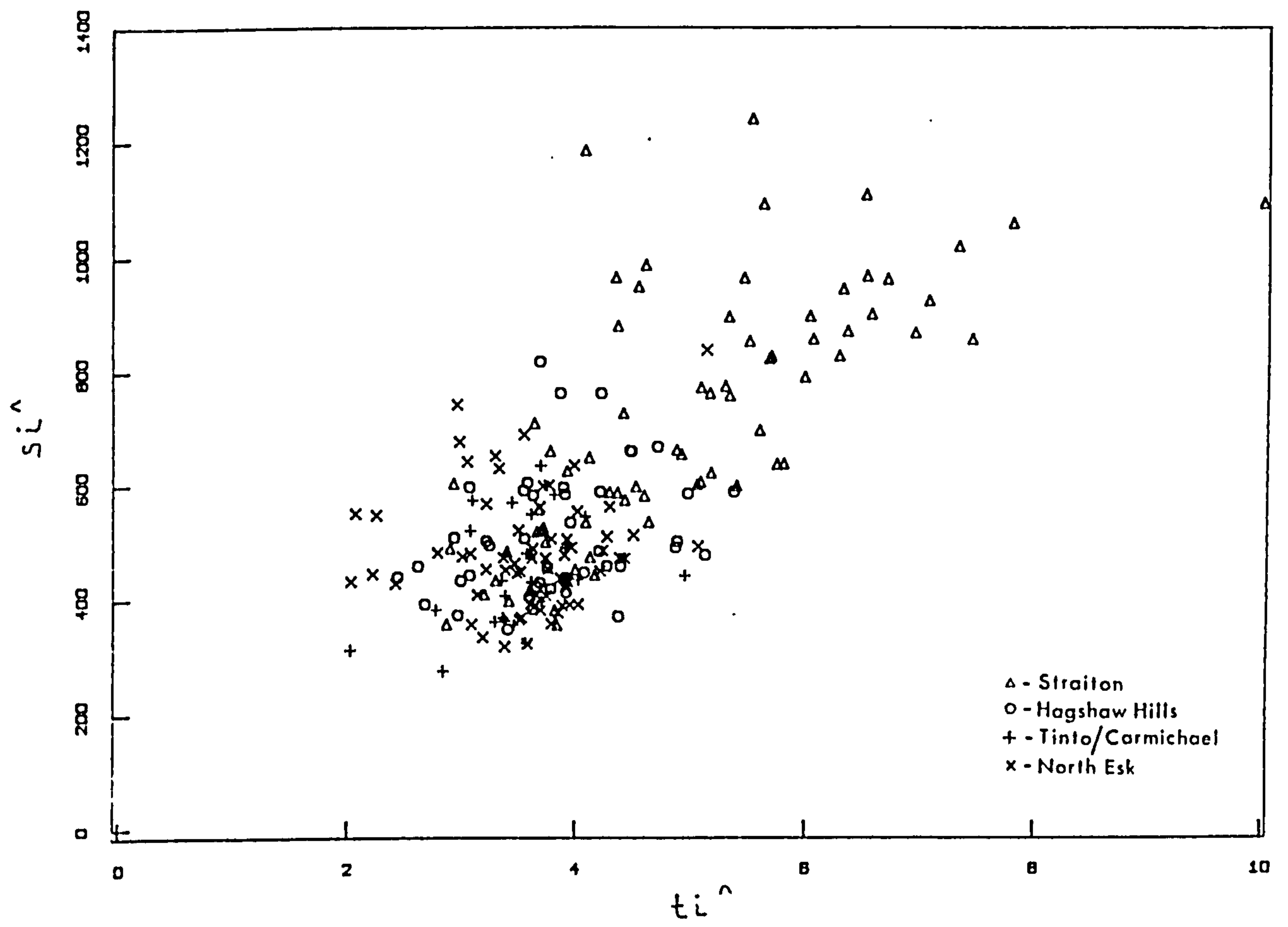


Fig. 5.3.18 $Si^$ vs $ti^$

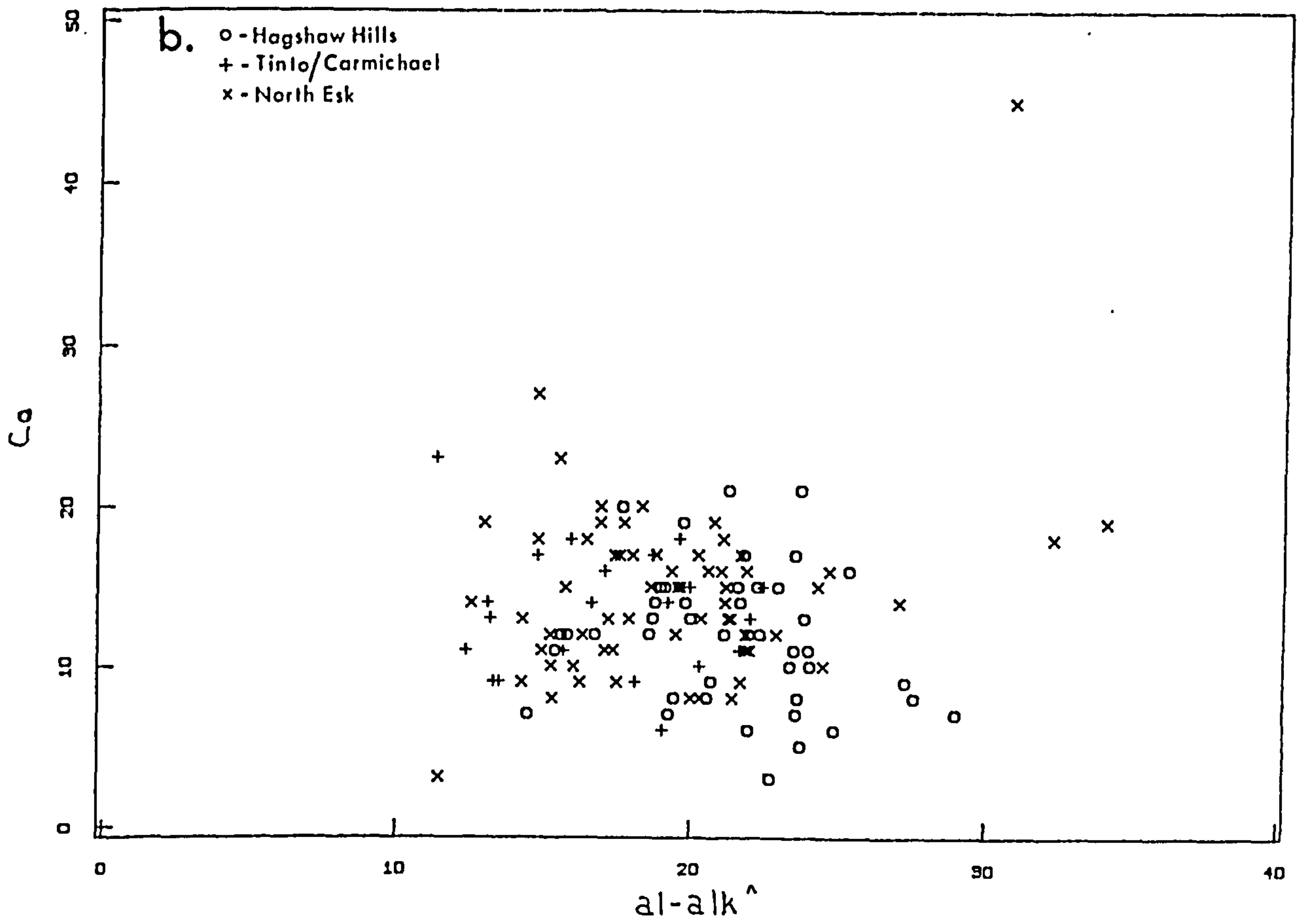
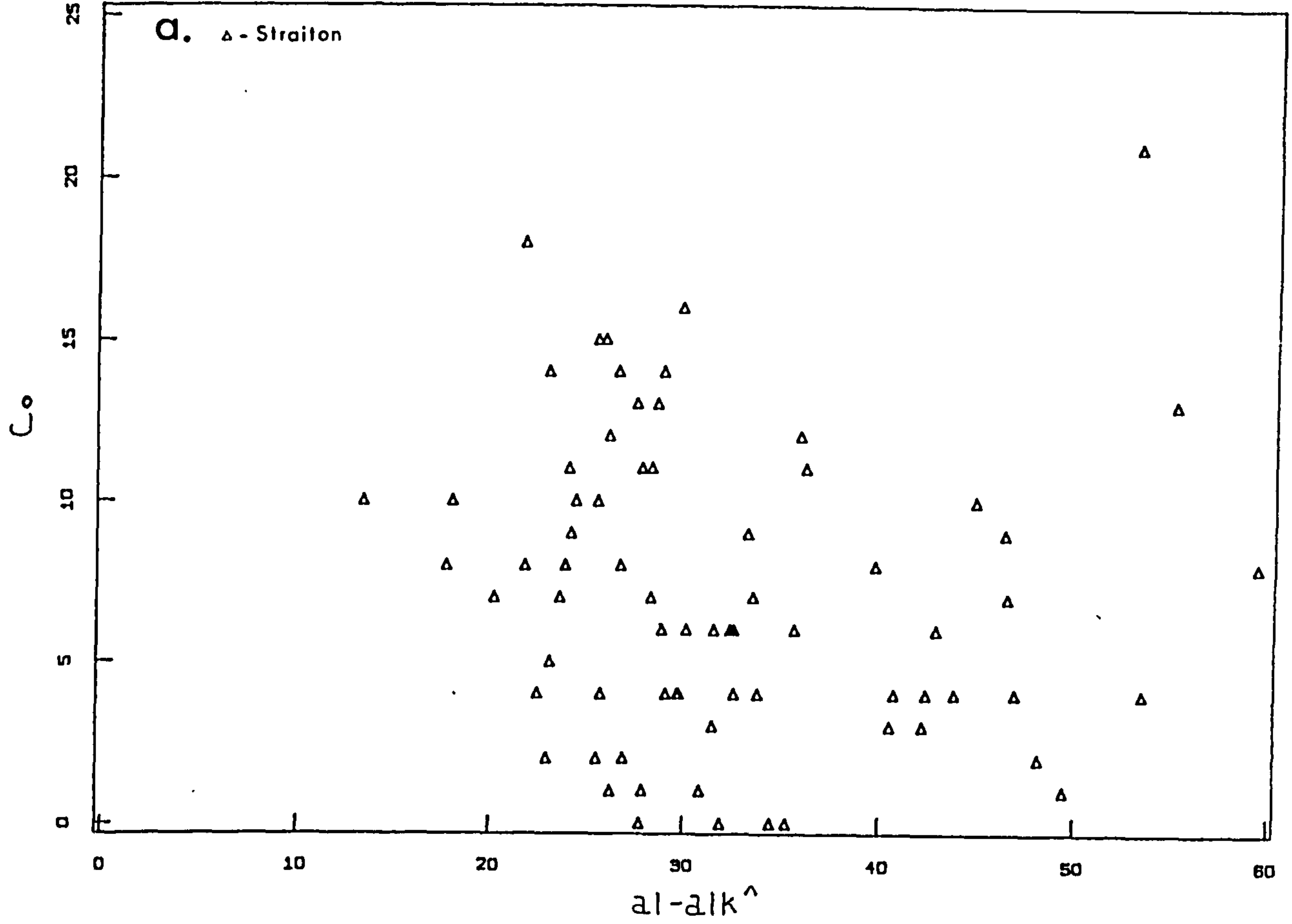


Fig. 5.3.19 (a-b) Co vs $al-alk^+$

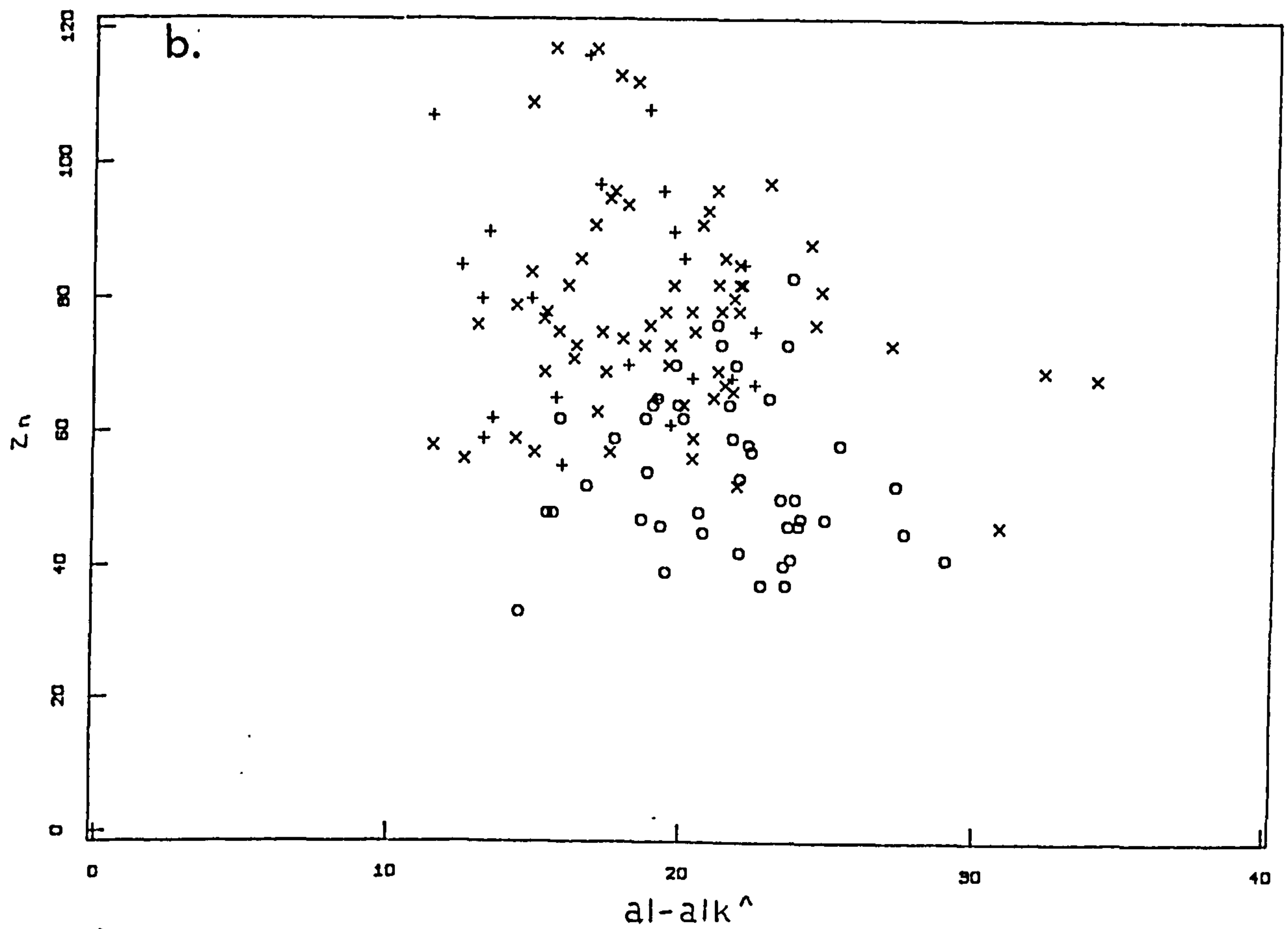
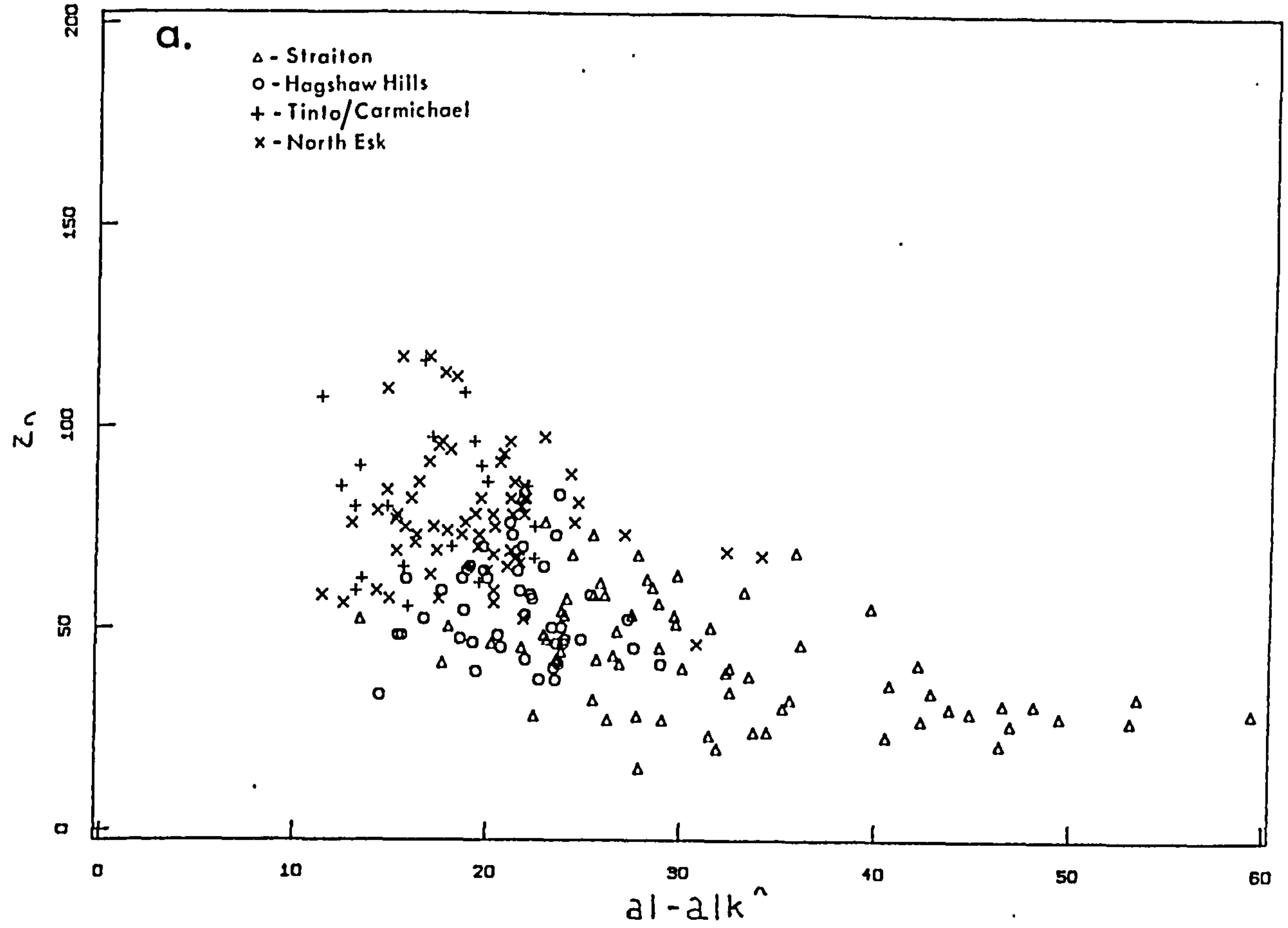


Fig. 5.3.20 (a-b) zn vs al^+-alk^+

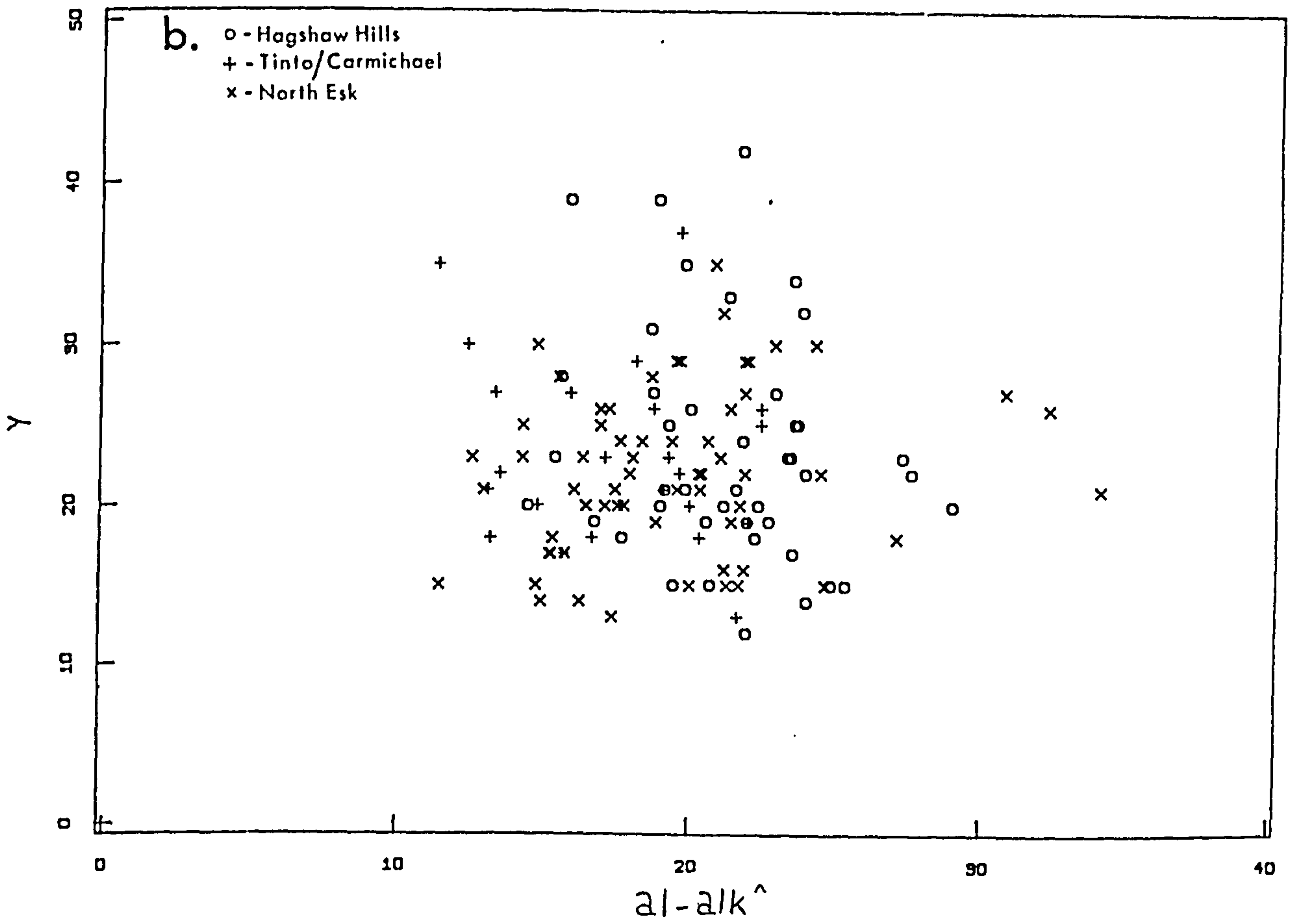
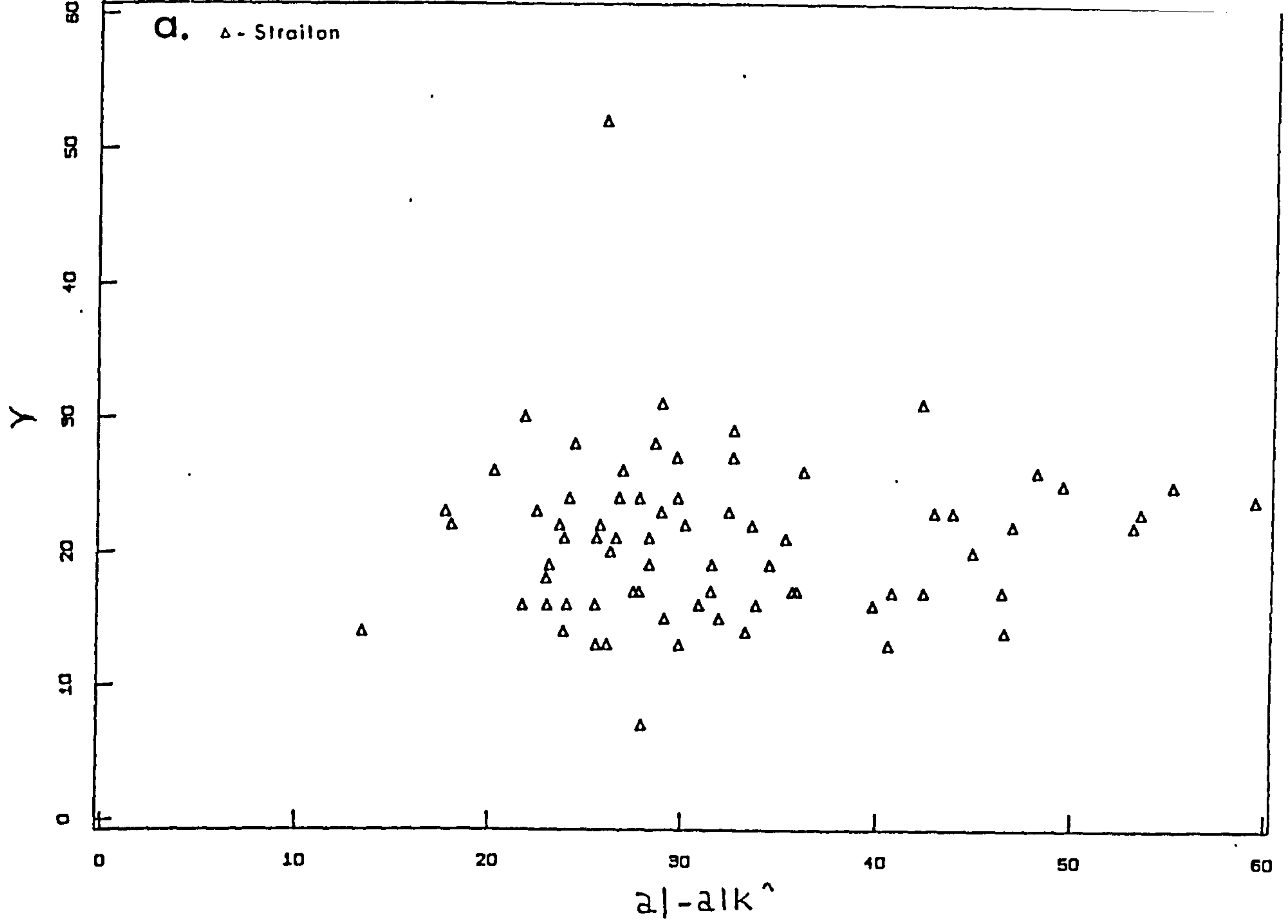


Fig. 5.3.21 (a-b) Y vs al[^]-alk[^]

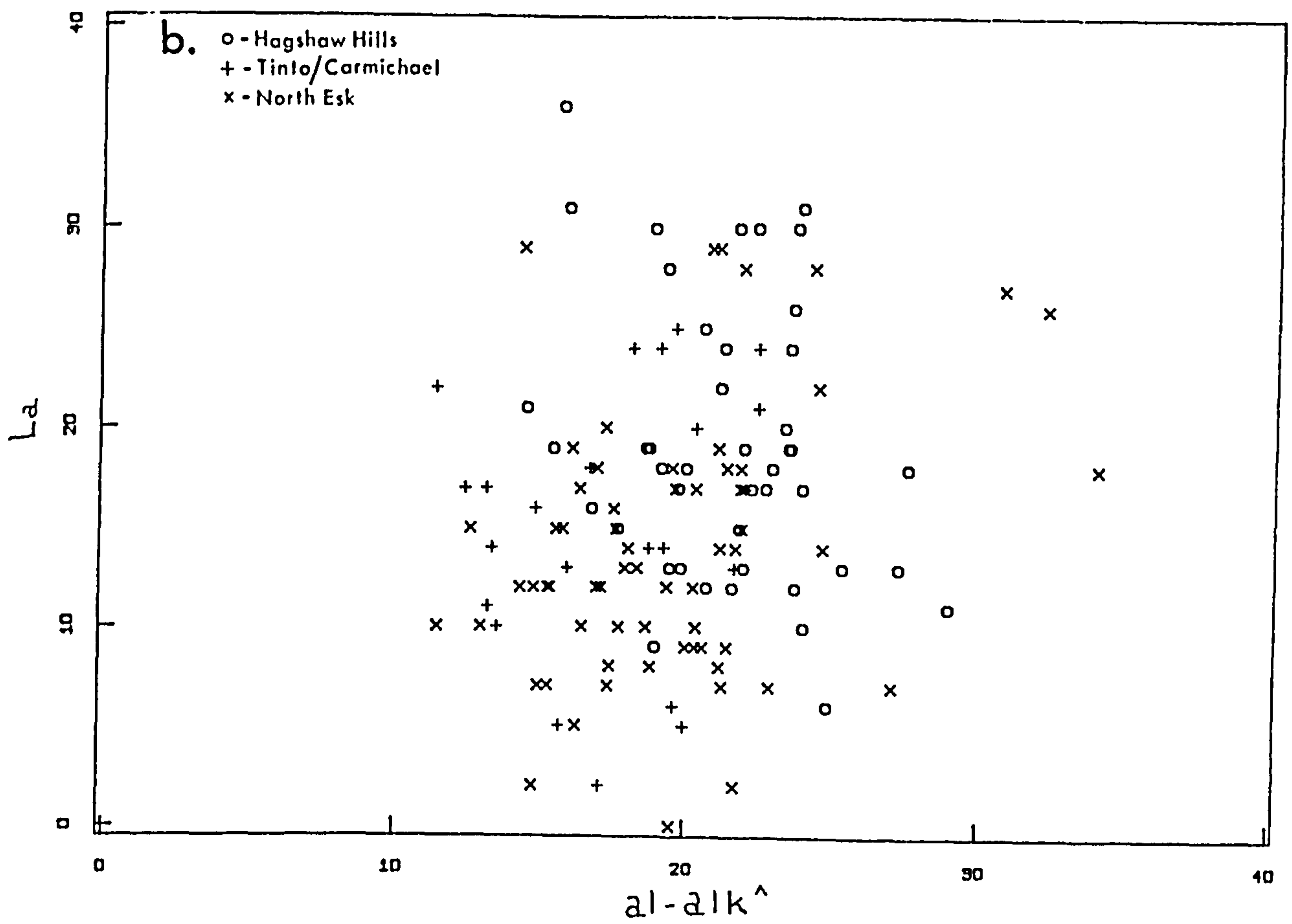
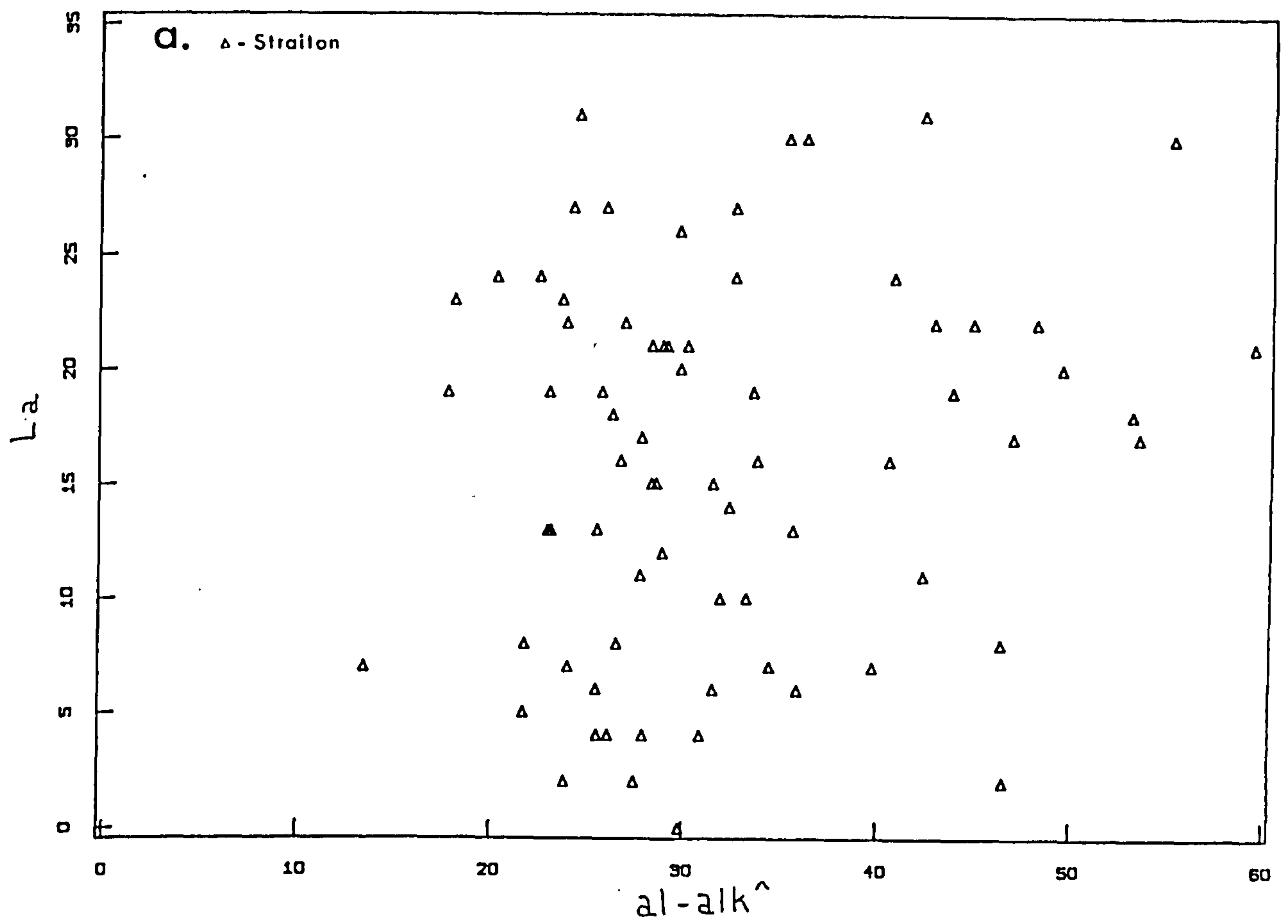


Fig. 5.3.22 (a-b) la vs al^+-alk^+

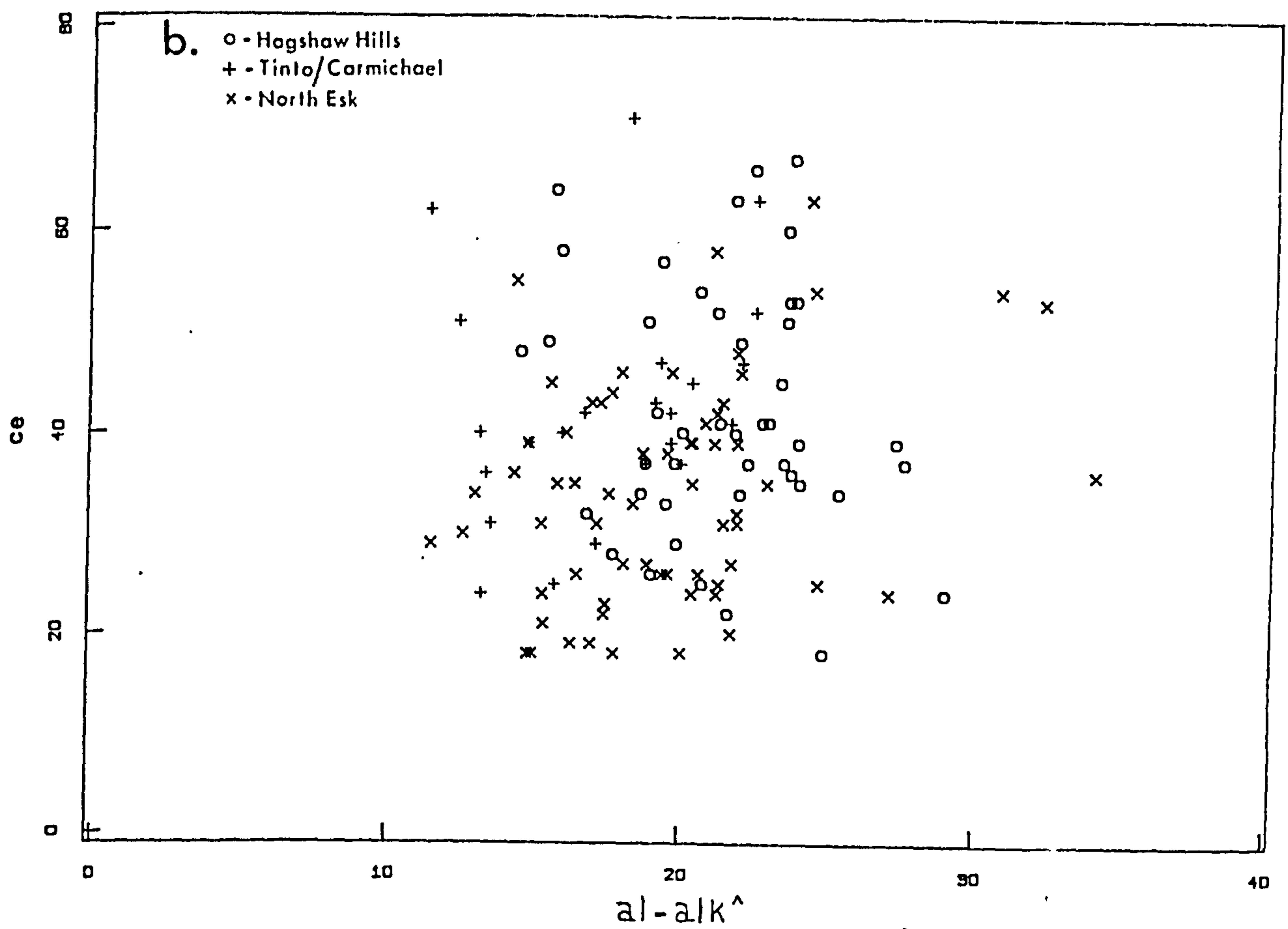
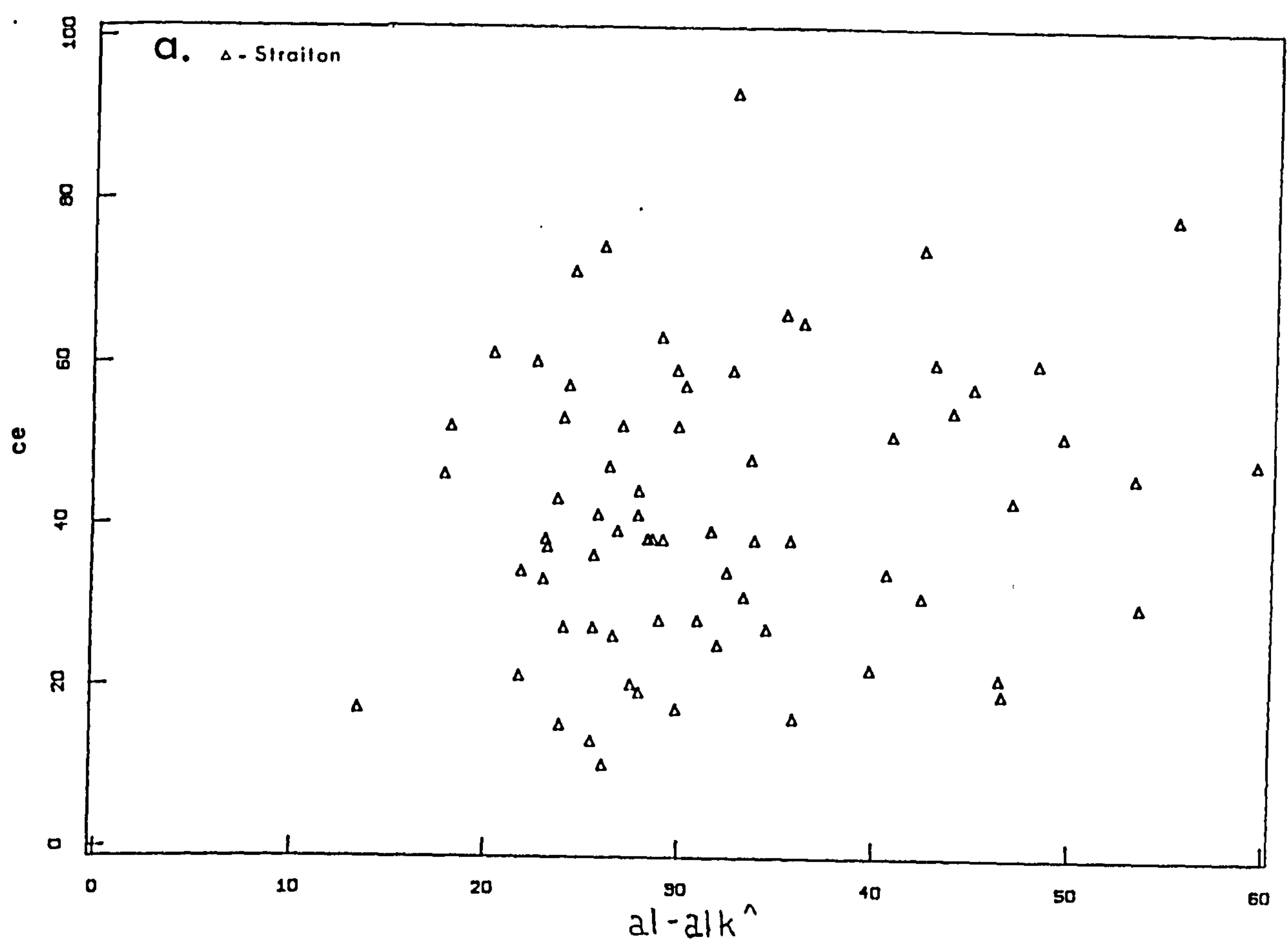


Fig. 5.3.23 (a-b) ce vs al[^]-alk[^]

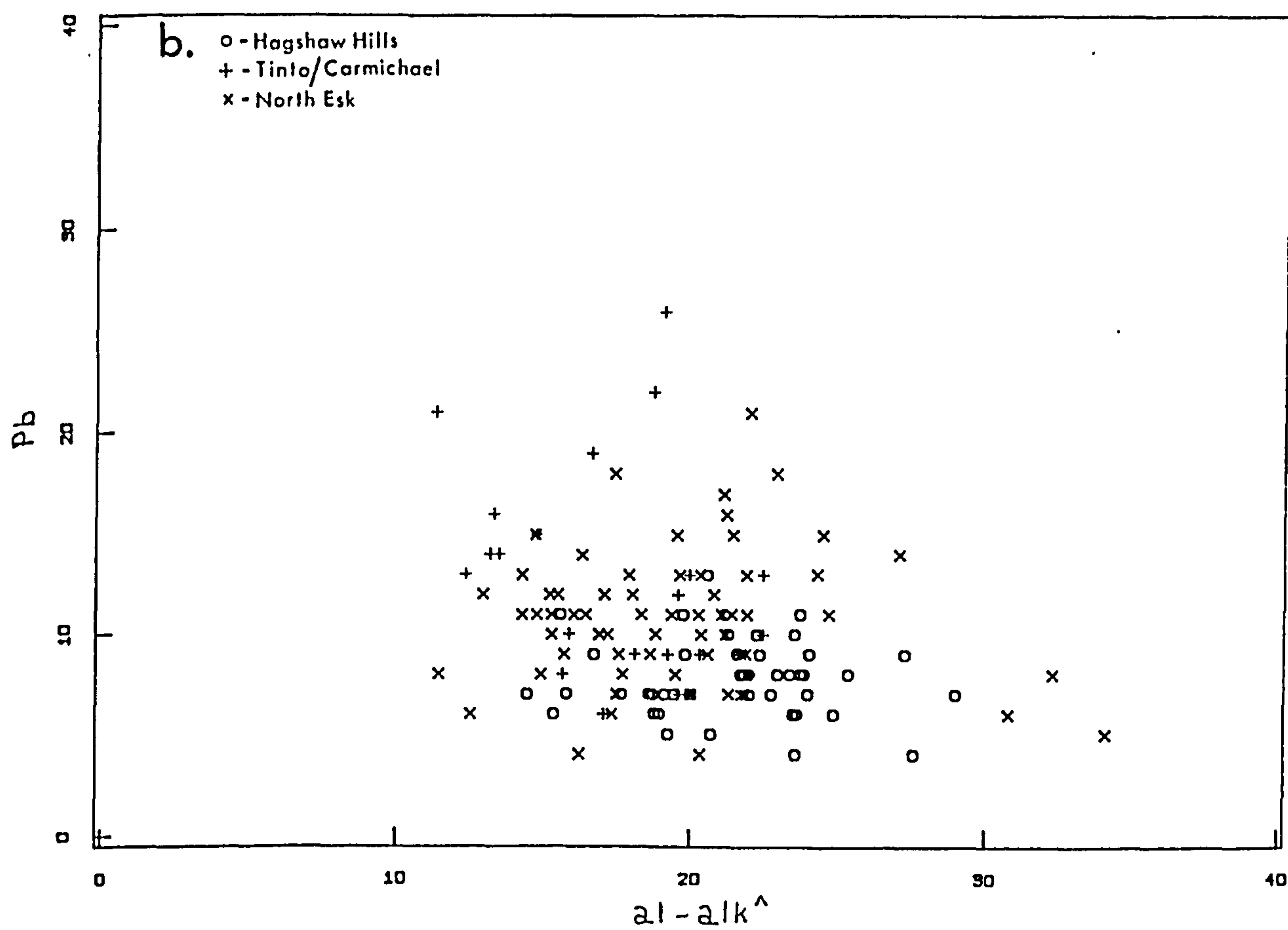
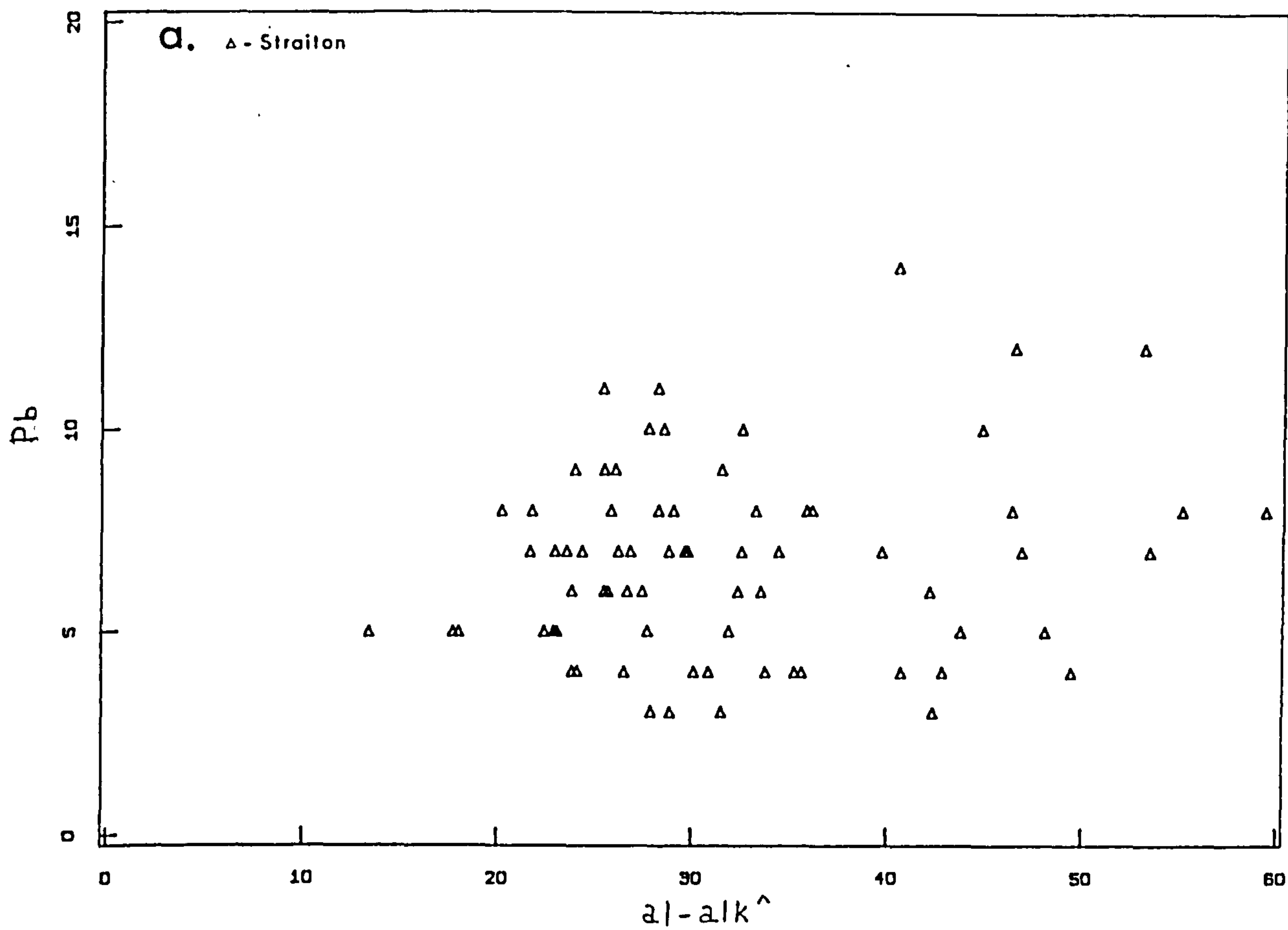


Fig. 5.3.24 (a-b) Pb vs $al-alk^+$

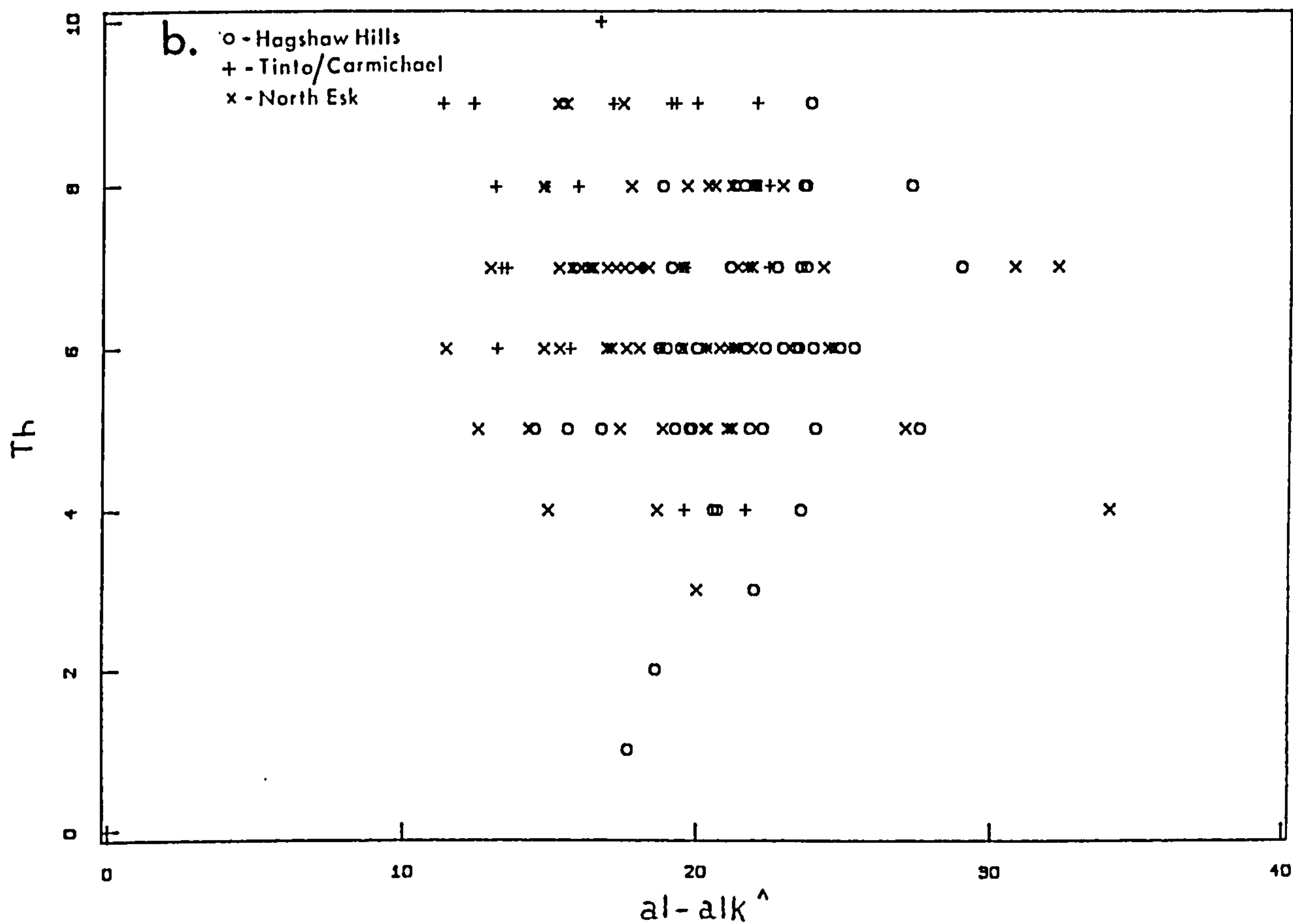
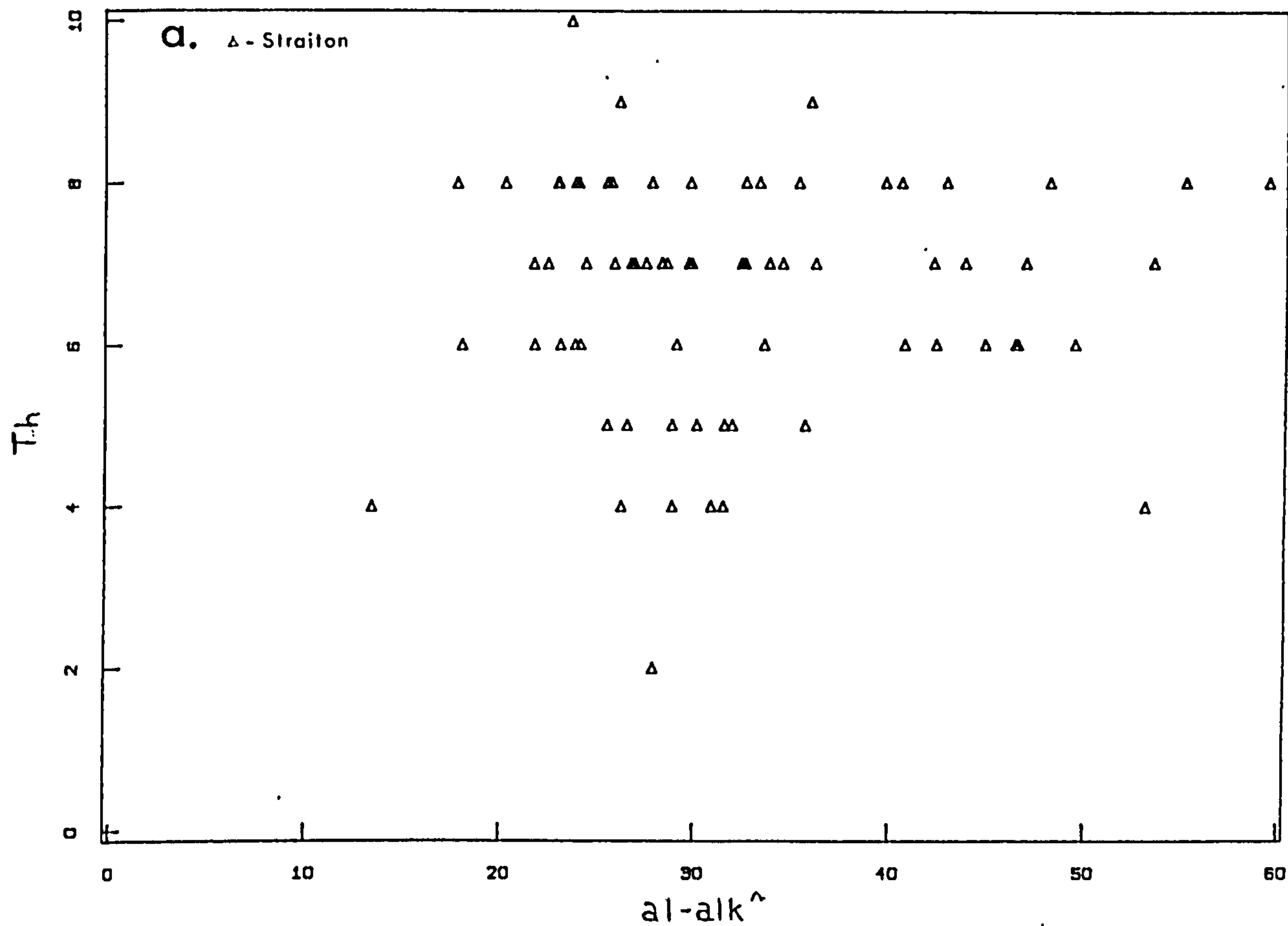


Fig. 5.3.25 (a-b) th vs $al-alk^$

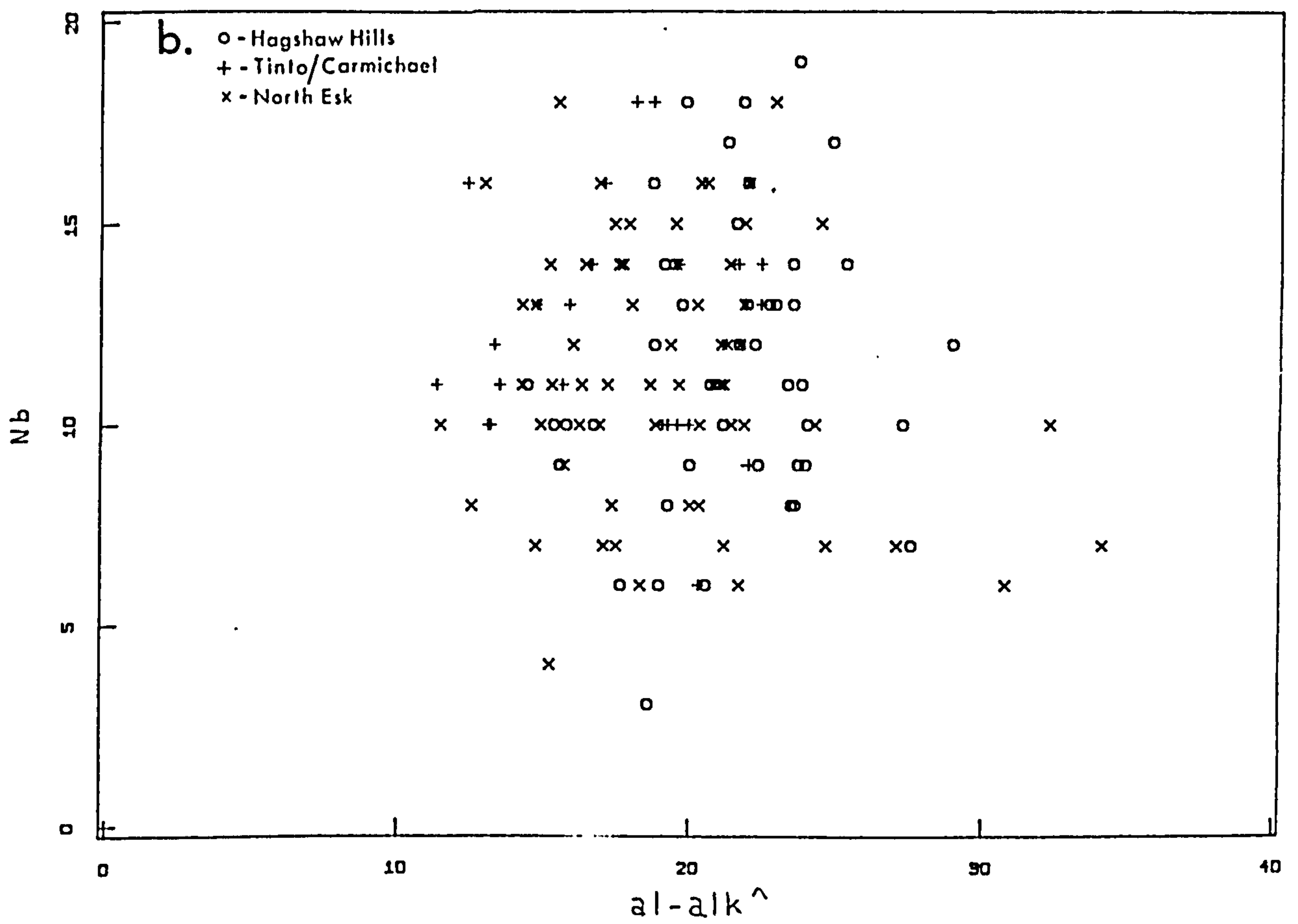
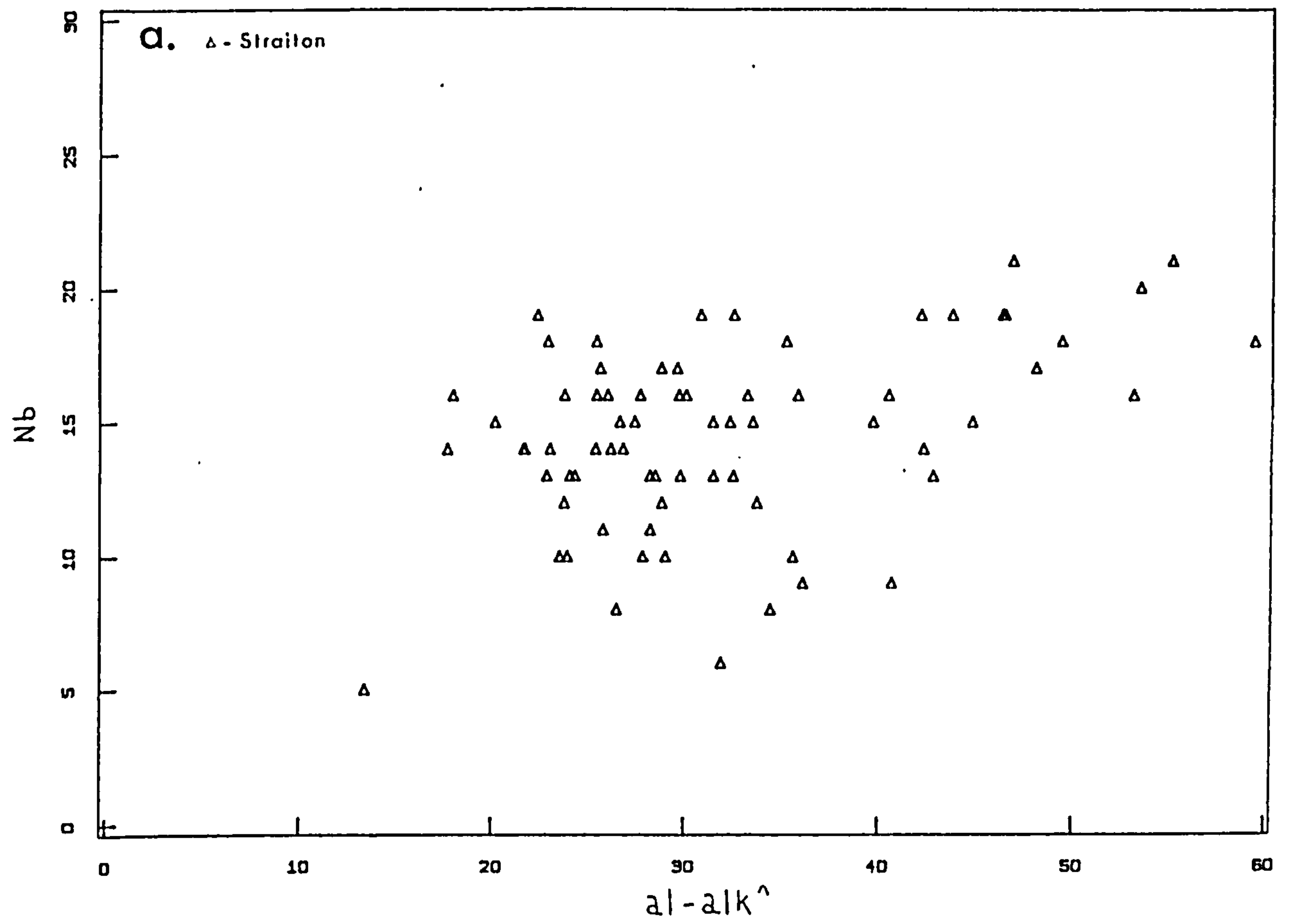
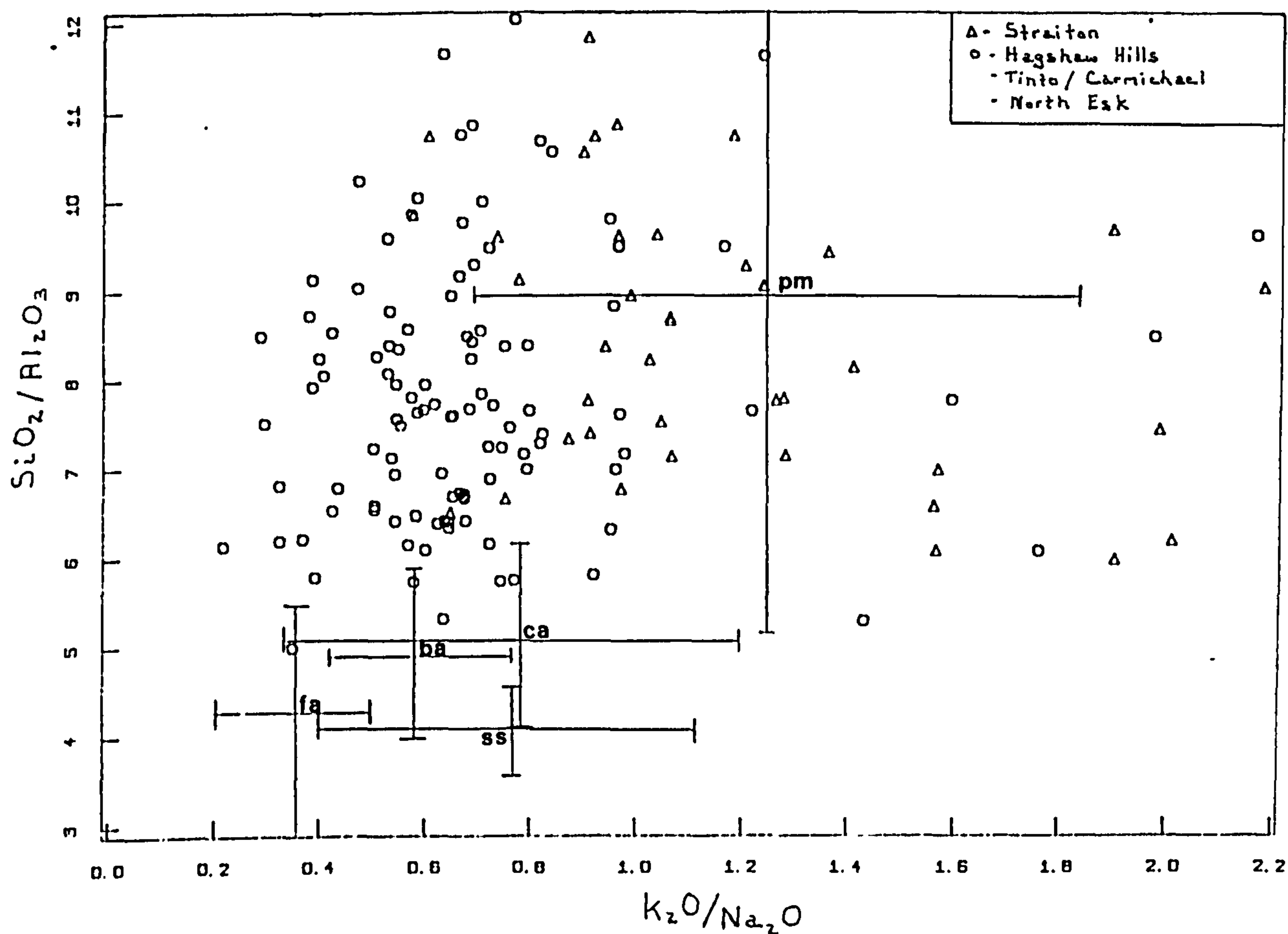


Fig. 5.3.26 (a-b) nb vs al^+-alk^+



pm-passive margin

ca-continental island arc

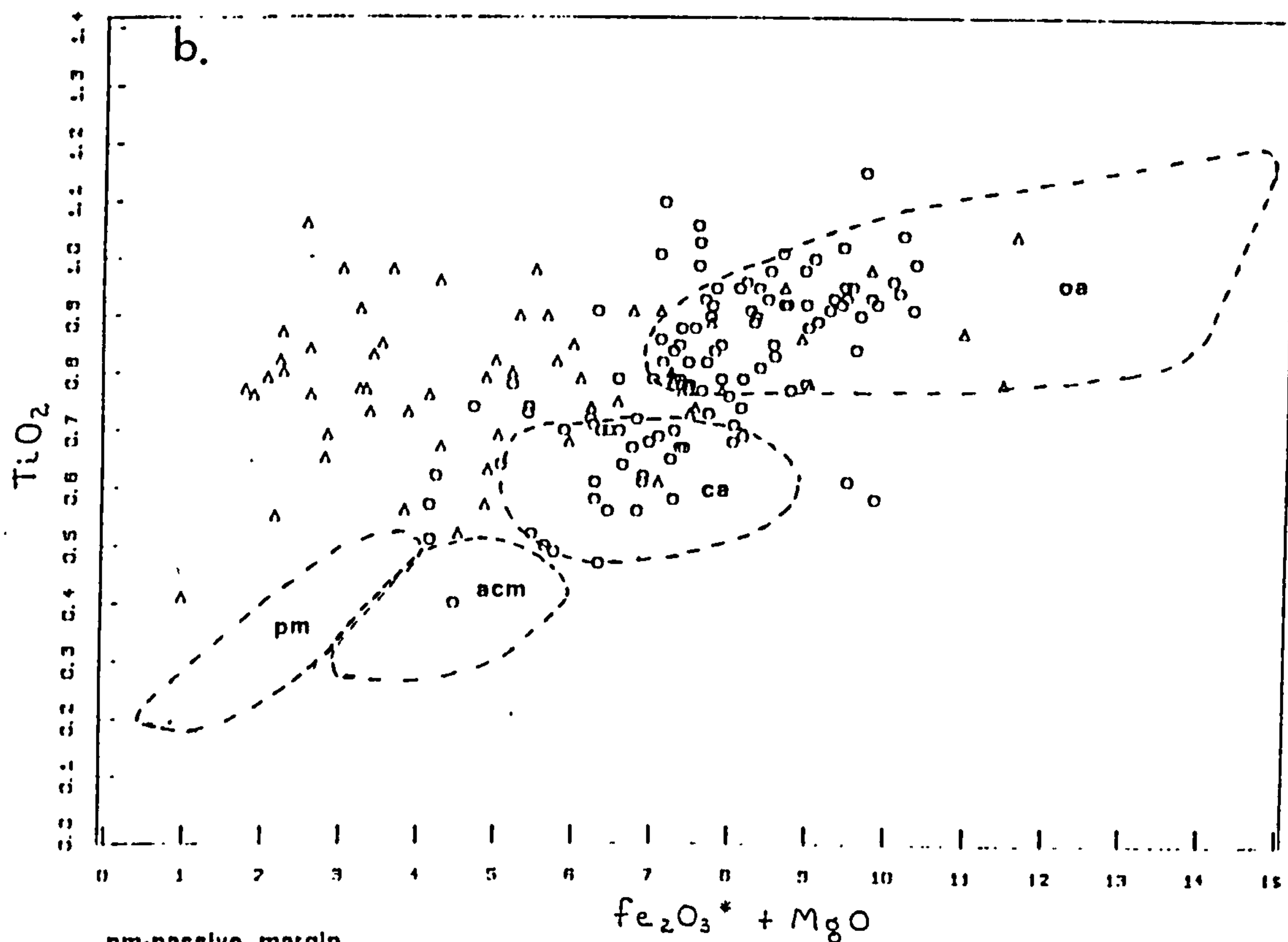
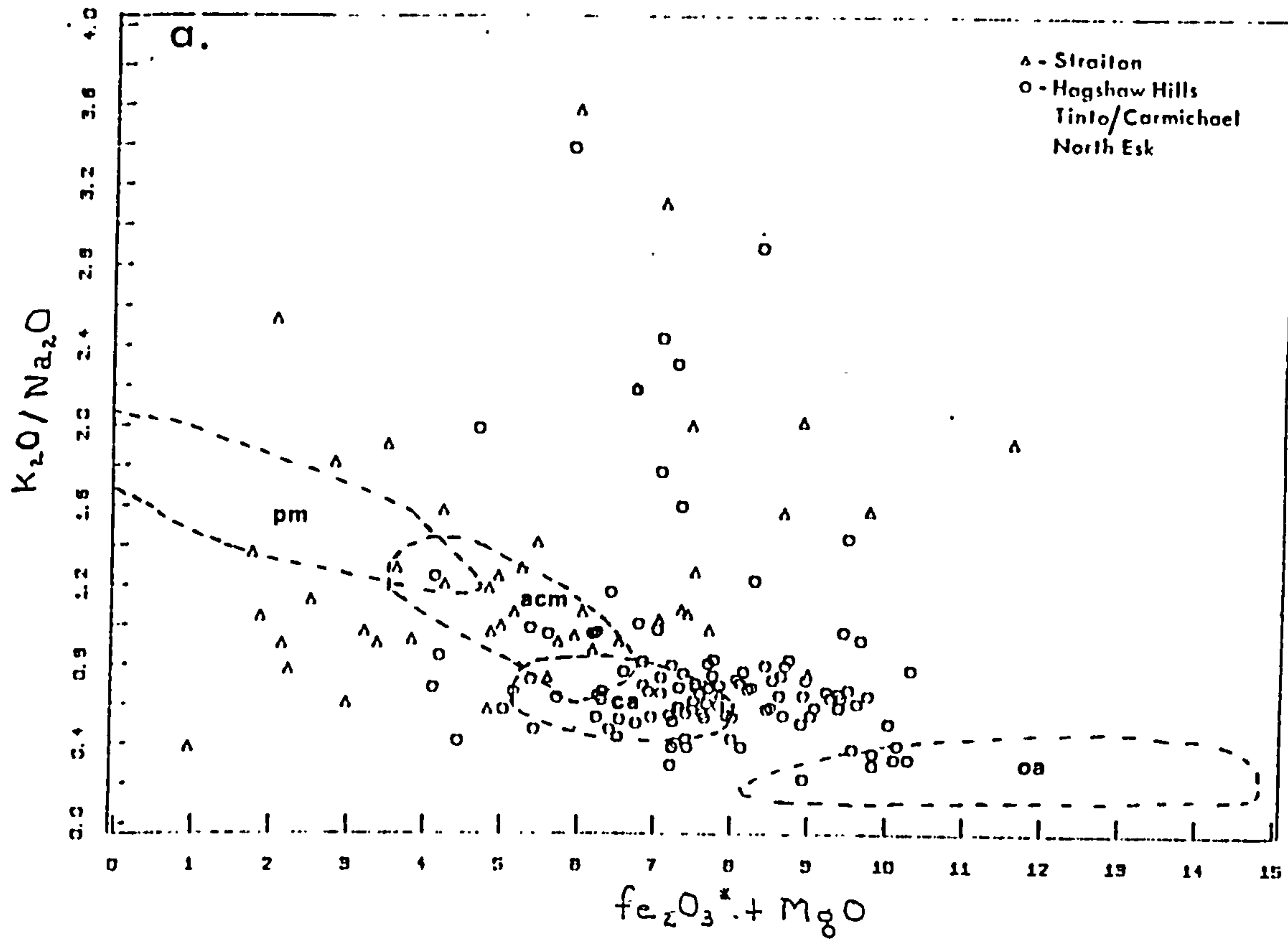
fa-fore-arc

ba-back arc

ss-strike slip

Fig. 5.4.1 Comparison of Greywacke Conglomerate ss clasts with modern sands from various tectonic settings.

note: values in excess of $\text{K}_2\text{O}/\text{Na}_2\text{O} > 2.2$ & $\text{SiO}_2/\text{Al}_2\text{O}_3 > 12$ not shown



pm-passive margin
acm-active continental margin
ca-continental arc
oa-oceanic arc

Fig. 5.4.2 (a-b) Comparison of Midland Valley ss clasts with ancient ss of known tectonic setting.

note: a). values in excess of $k_2o/na_2o > 4$ not shown

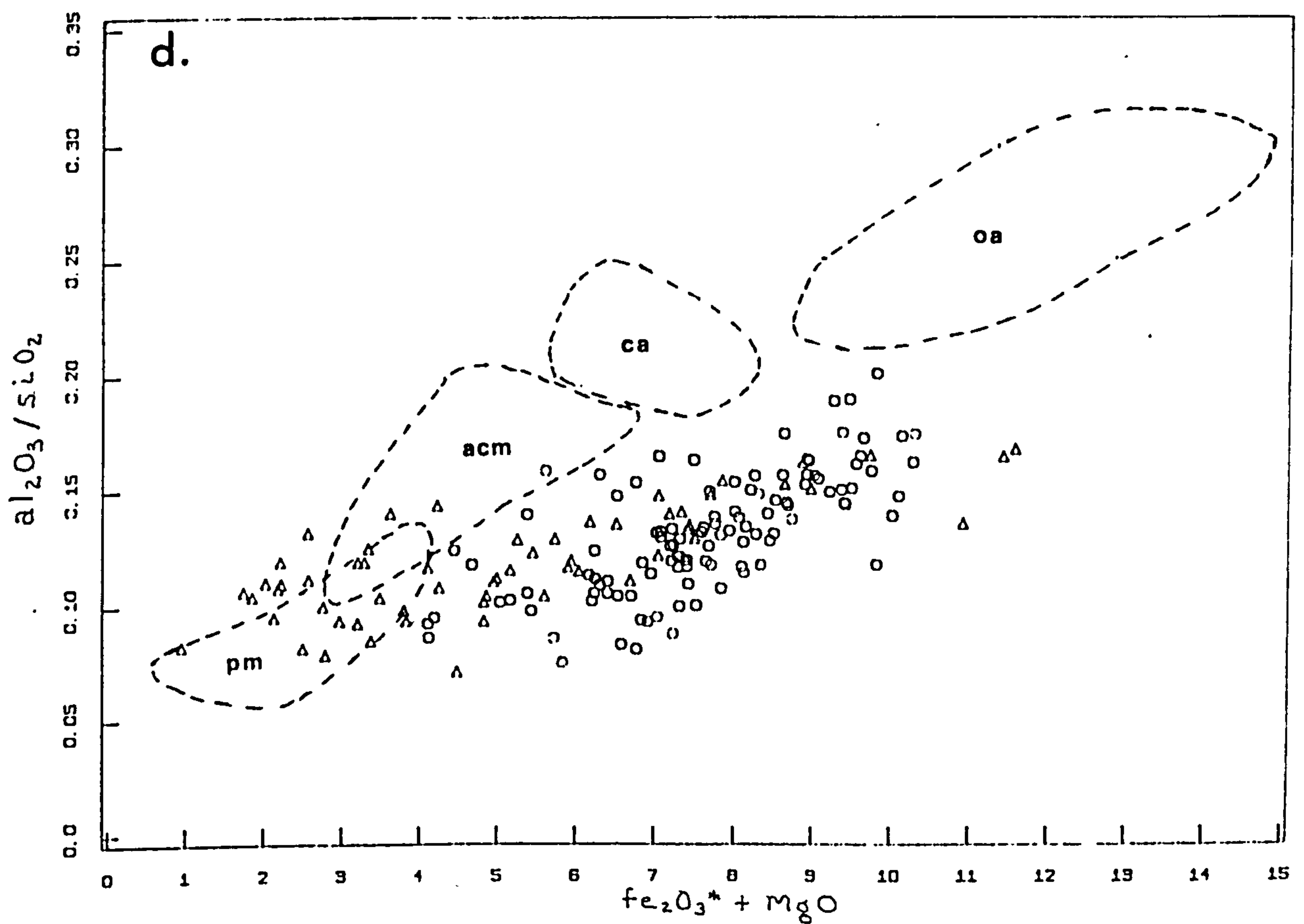
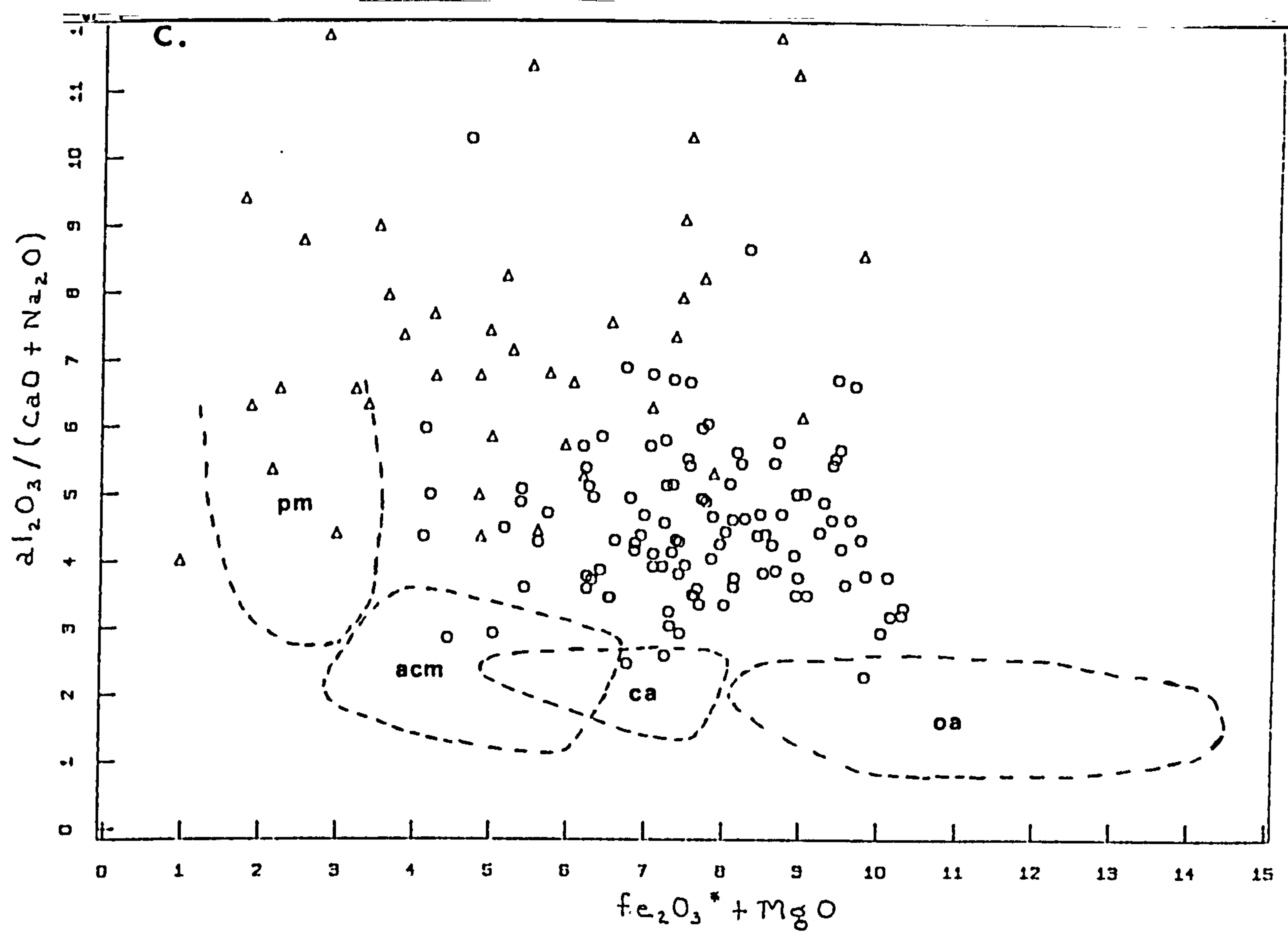


Fig. 5.4.2 (c-d) Comparison of Midland Valley ss clasts with ancient ss of known tectonic setting.

note: c). values in excess of $\text{Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O}) > 12$ not shown

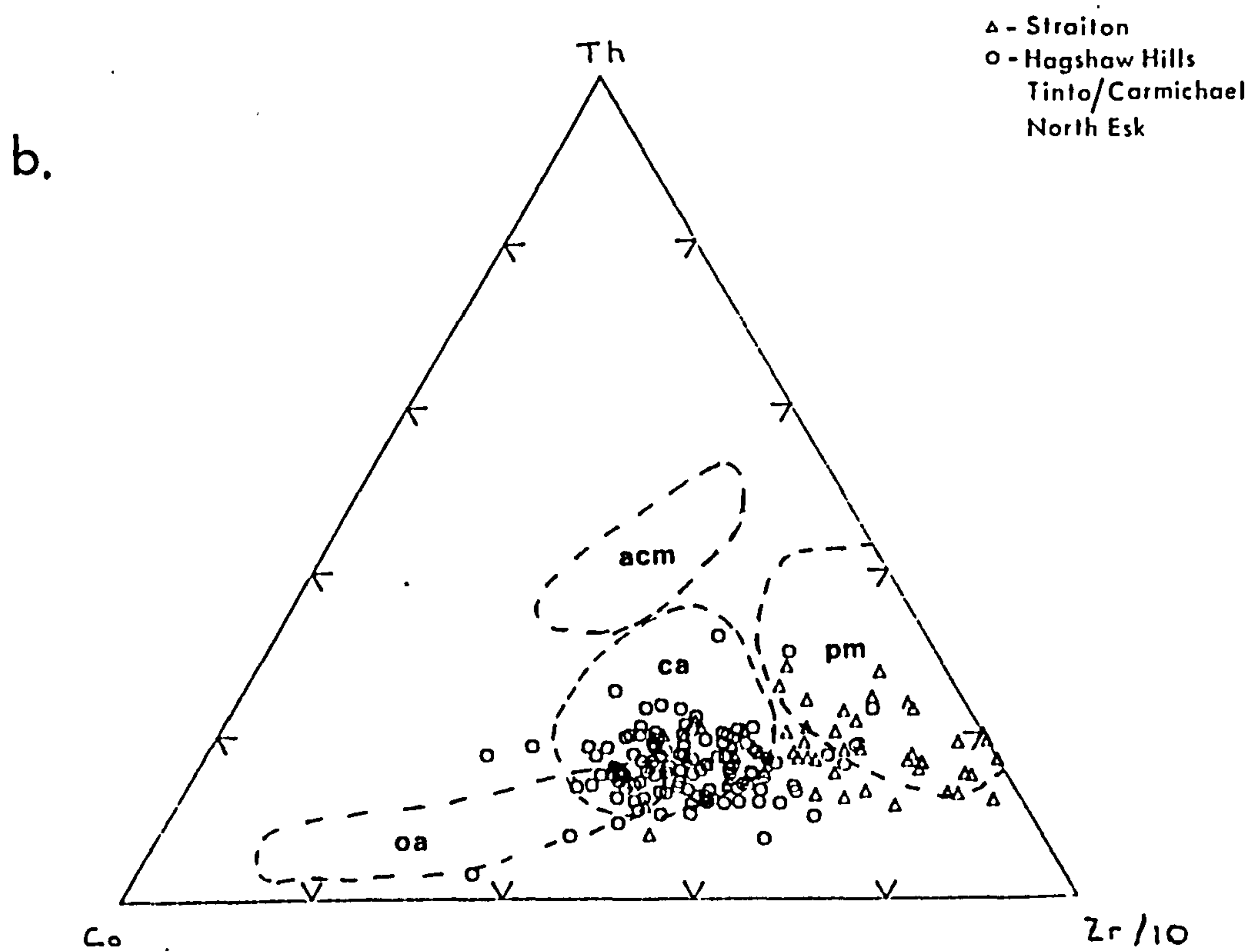
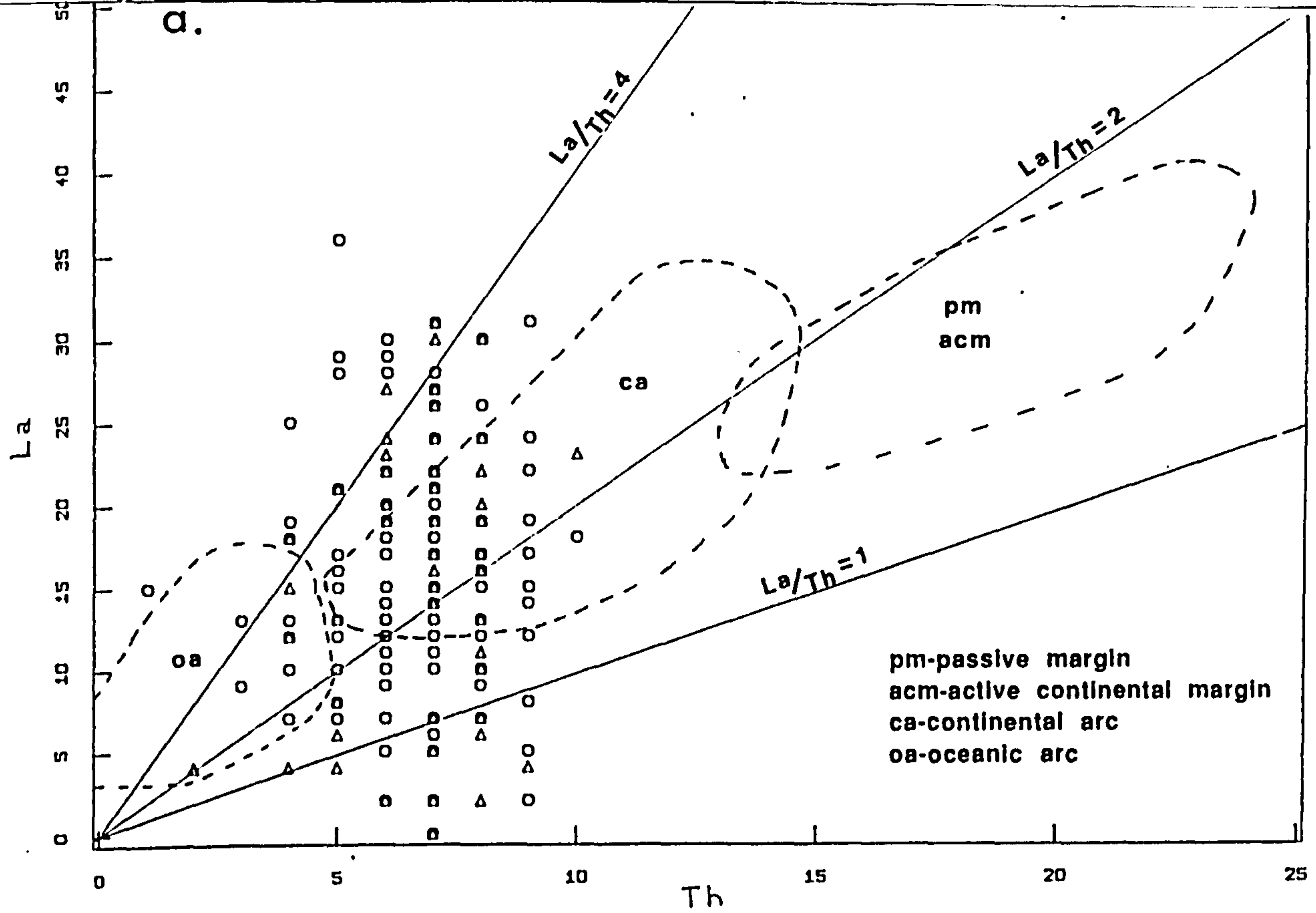


Fig. 5.4.3 (a-b) Comparison of Midland Valley ss clasts with ancient ss of known tectonic setting.

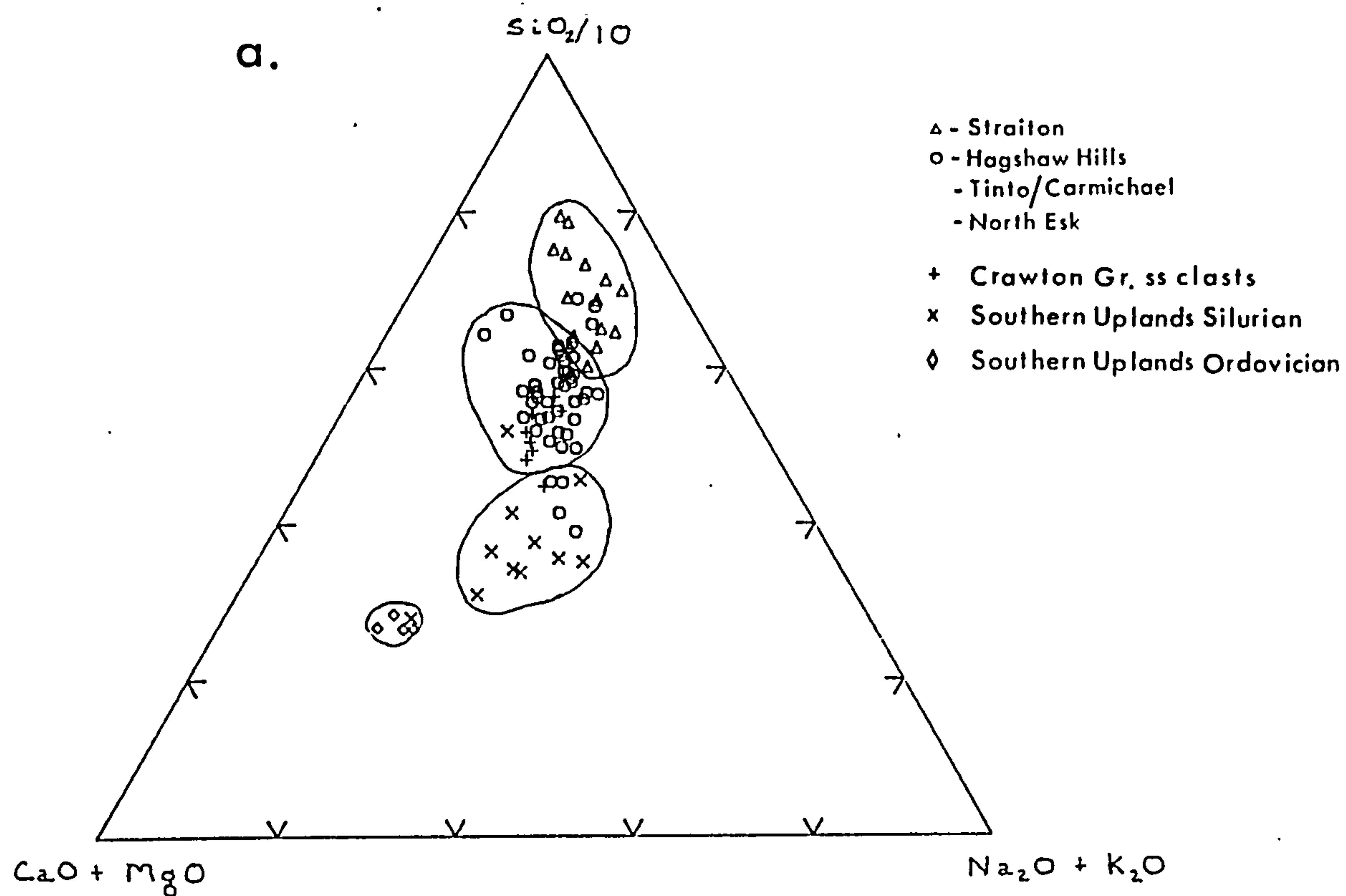


Fig. 5.4.4 (a) Comparison of Midland Valley ss clasts with Southern Uplands sediments and Crawton Group ss clasts.

note: Fig. 5.4.4 (a-e) 2 samples plotted with Silurian Southern Uplands are acid rich samples from Ord. close to the boundary between Northern (Ordovician) and Central (Silurian) Belts.

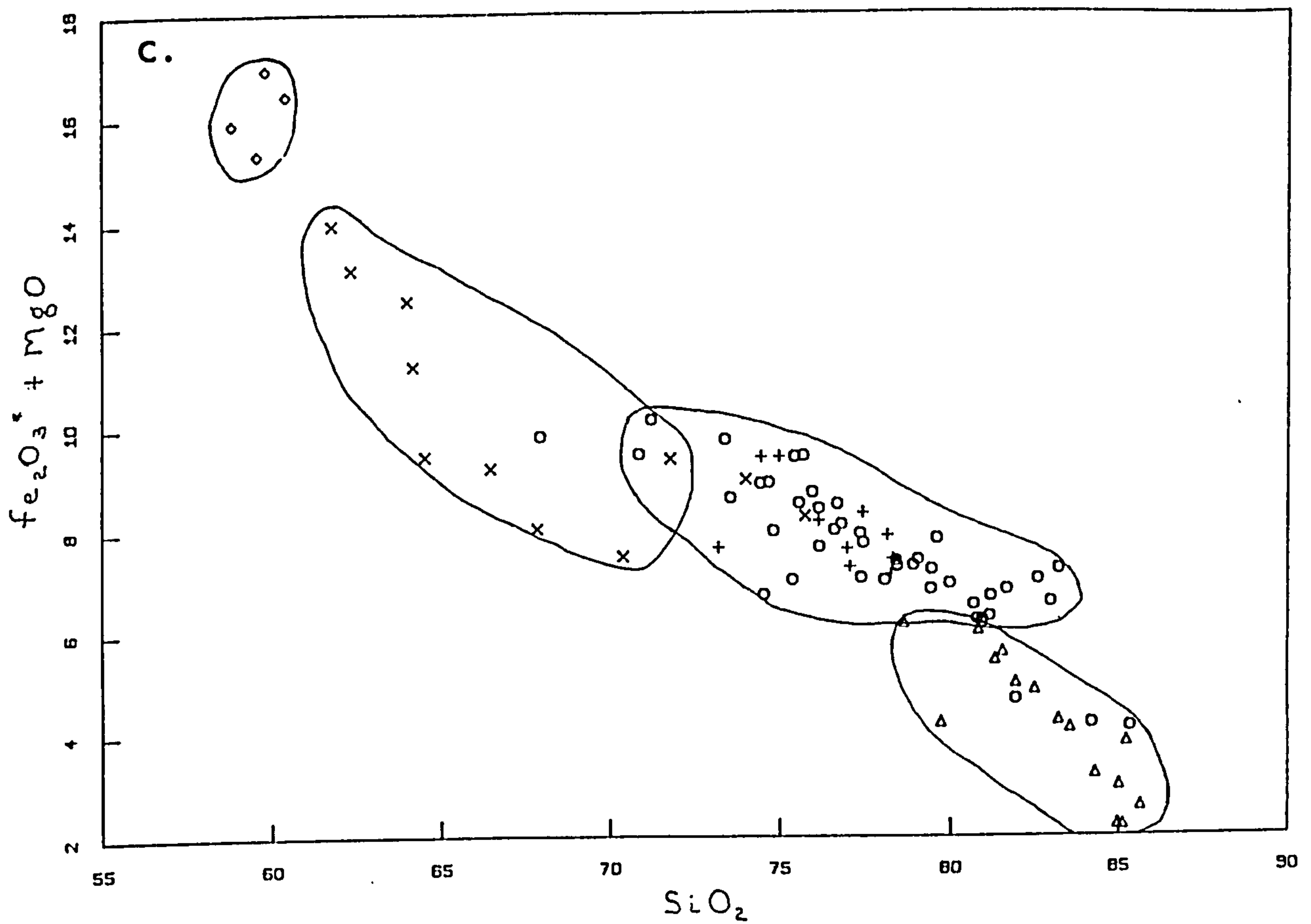
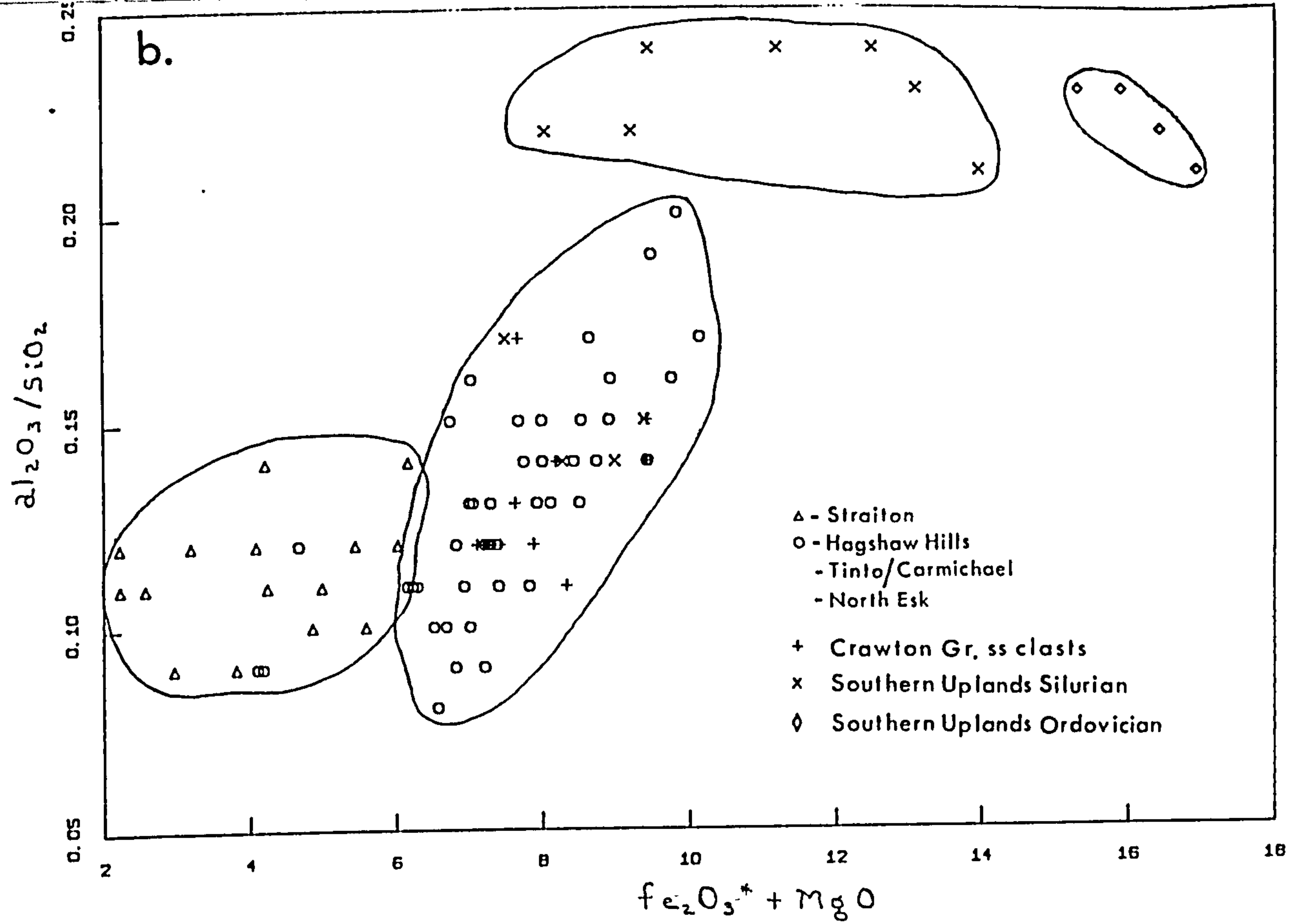


Fig. 5.4.4 (b-c) Comparison of Midland Valley ss clasts with Southern Uplands sediments and Crawton Group ss clasts.

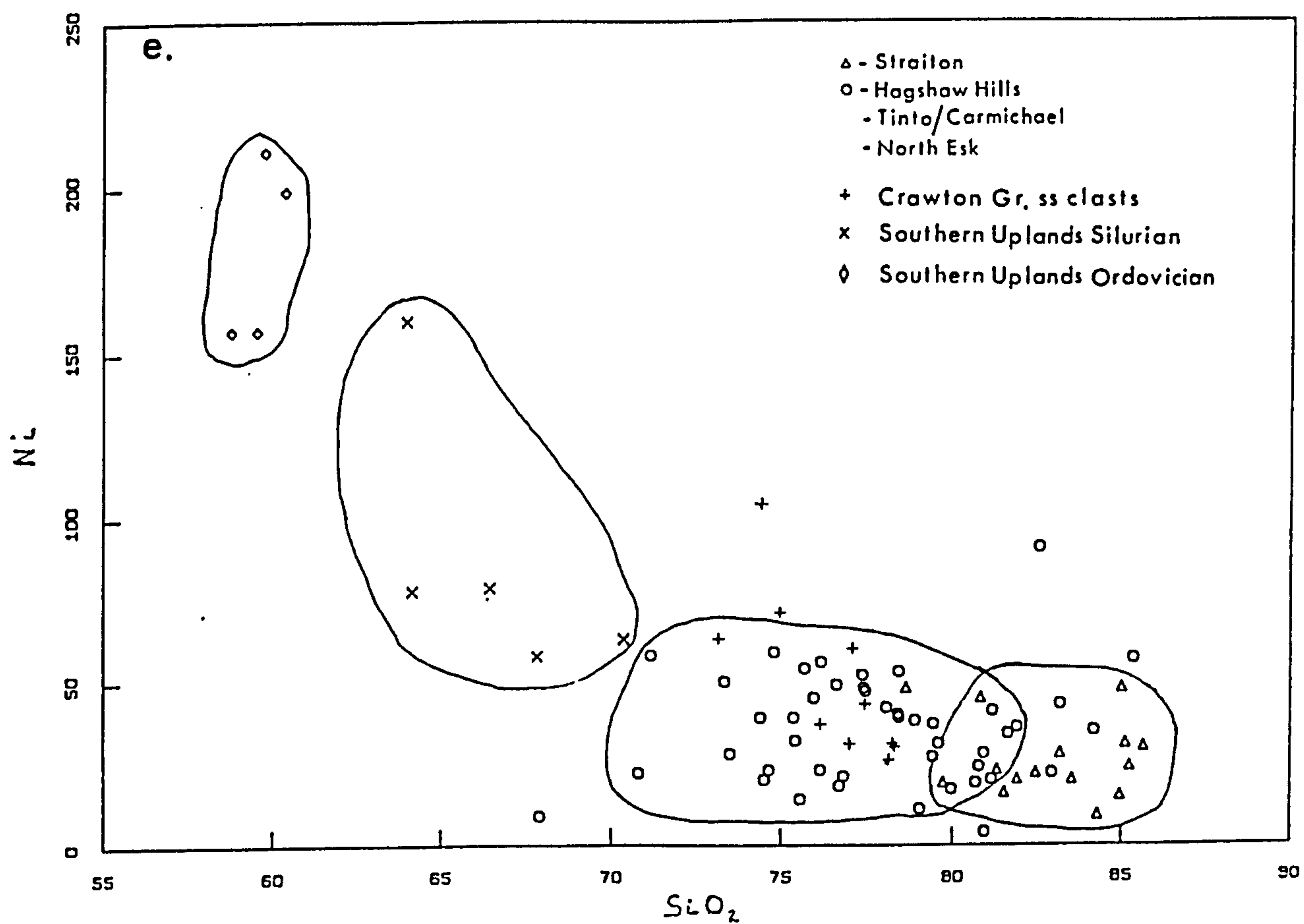
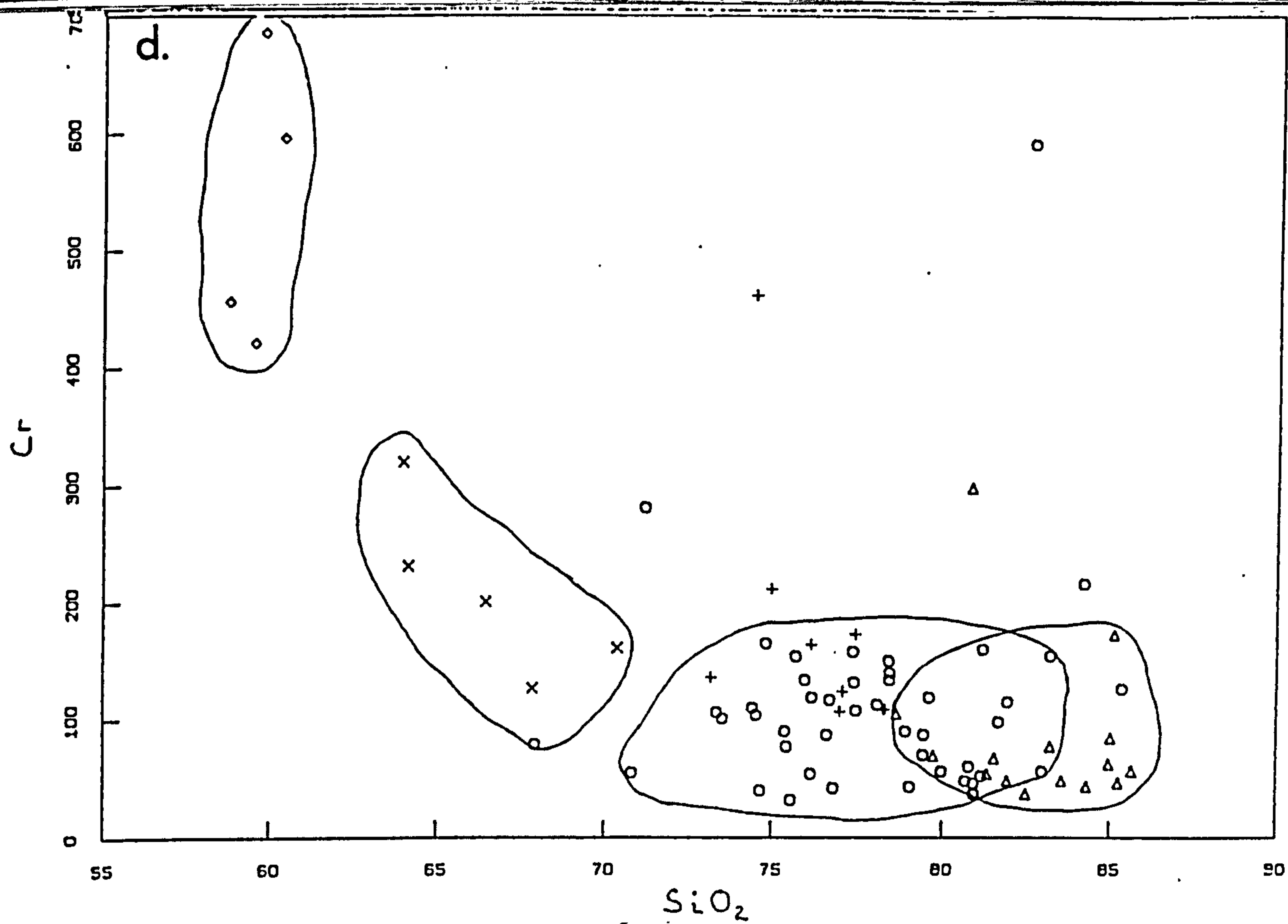


Fig. 5.4.4 (d-e) Comparison of Midland Valley ss clasts with Southern Uplands sediments and Crawton Group ss clasts.

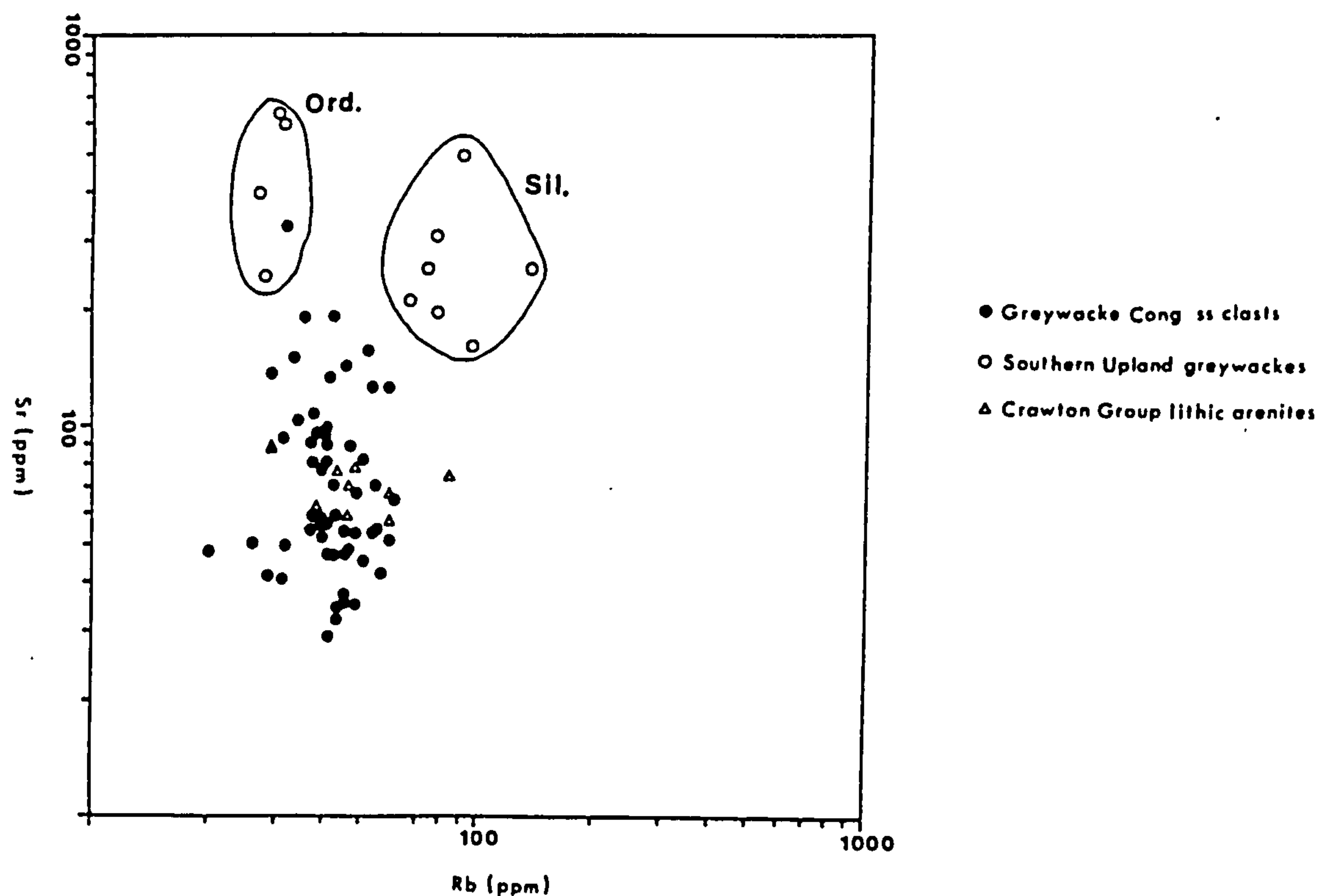
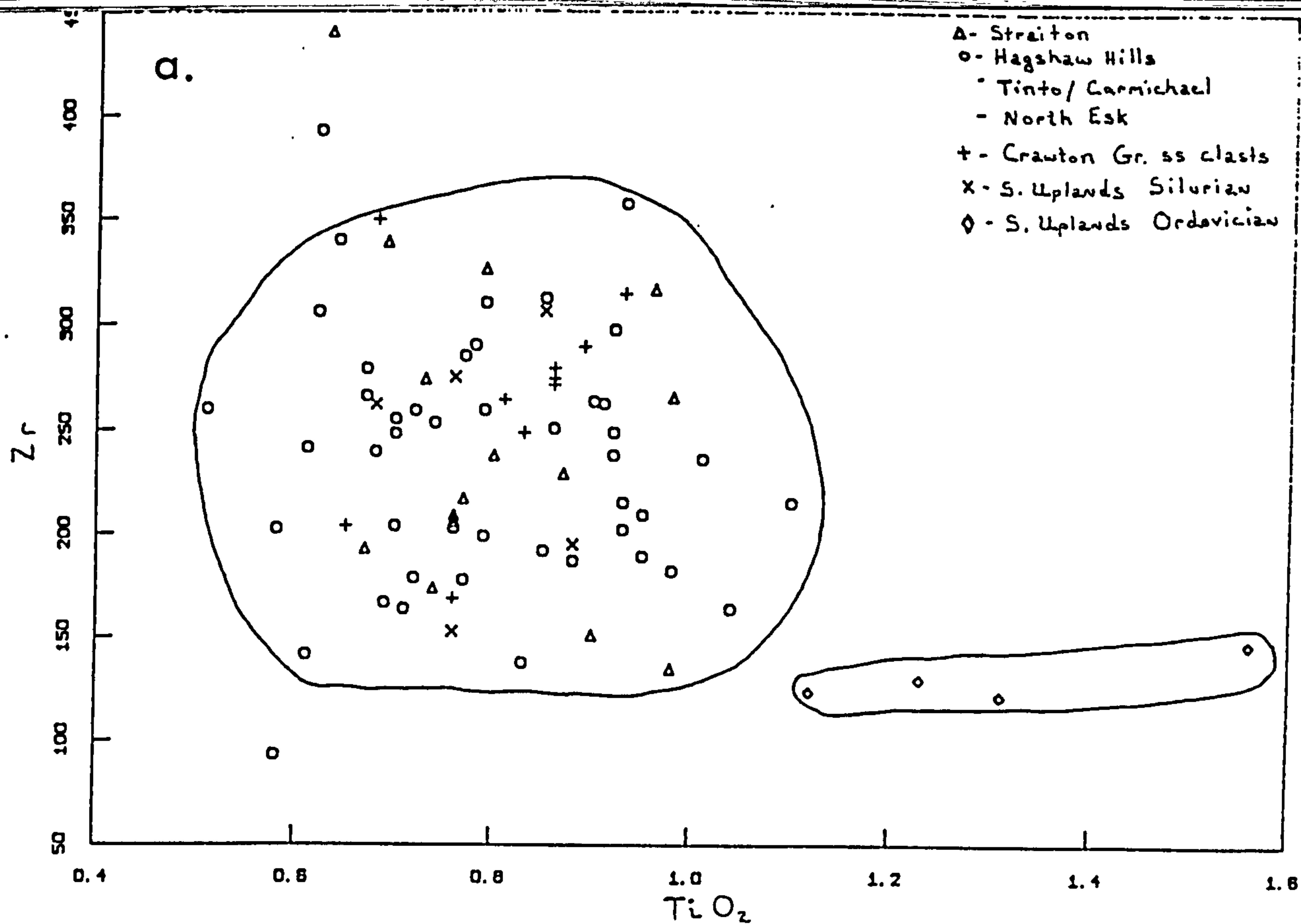


Fig. 5.4.5 (a-b) Comparison of Midland Valley ss clasts with Southern Uplands sediments and Crawton Group ss clasts.

note: Fig. 5.4.5 (a-b) 2 samples plotted with Silurian Southern Uplands are acid rich samples from Ord. close to the boundary between Northern (Ordovician) and Central (Silurian) Belts.

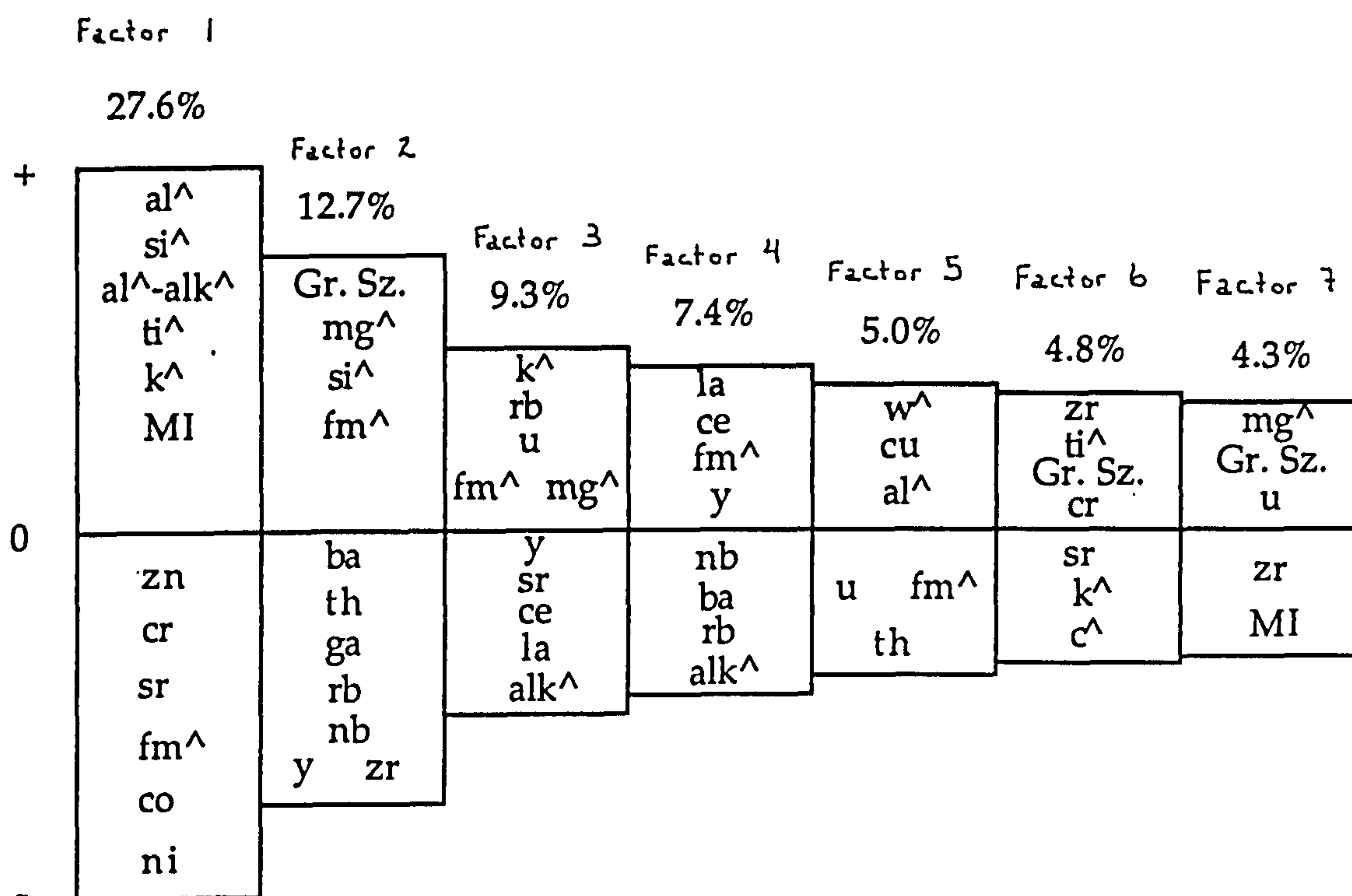


Fig. 5.5.1 Schematic diagram of first seven principal component factors

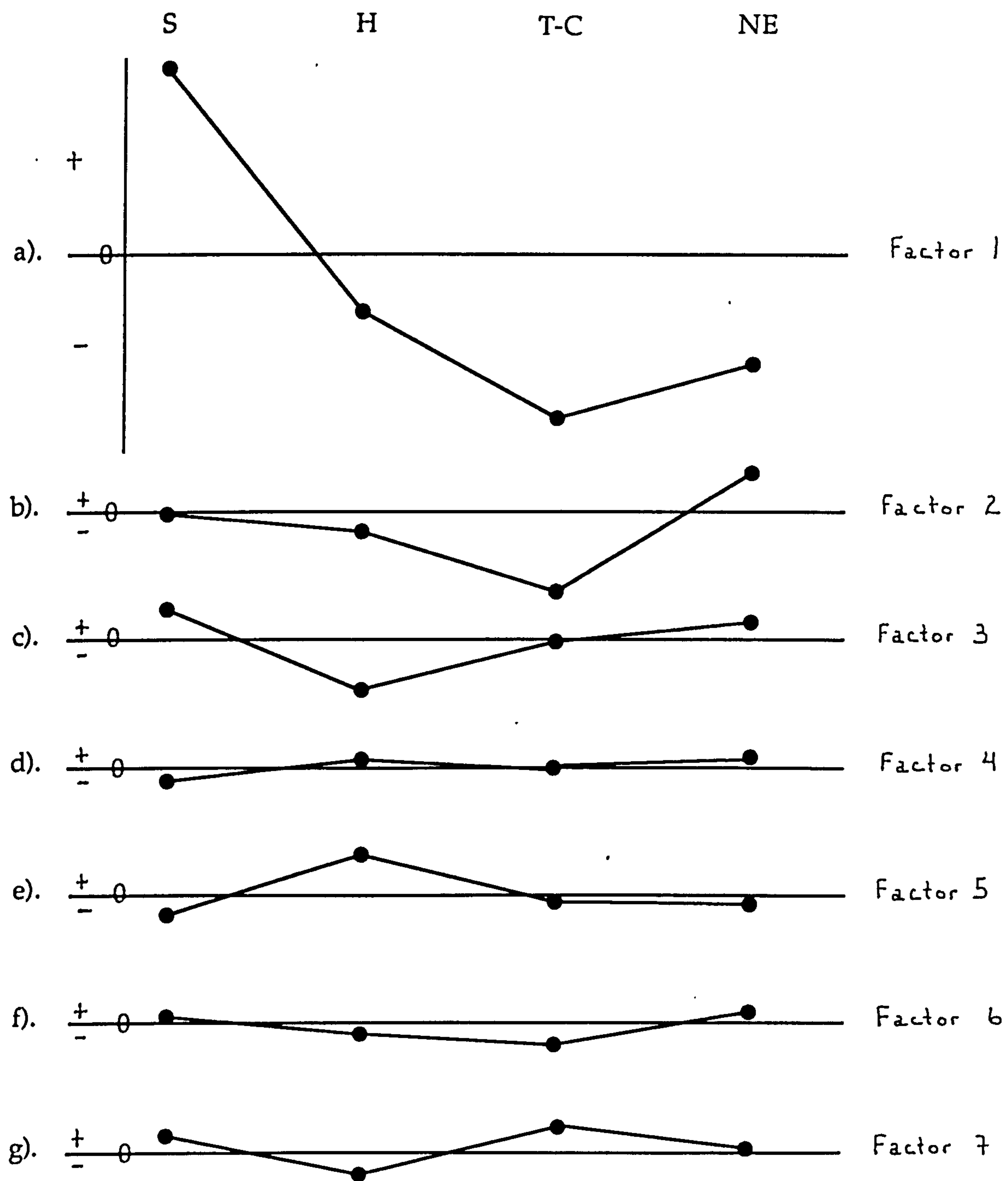


Fig. 5.5.2 Lateral geochemical trends for Midland Valley Conglomerates

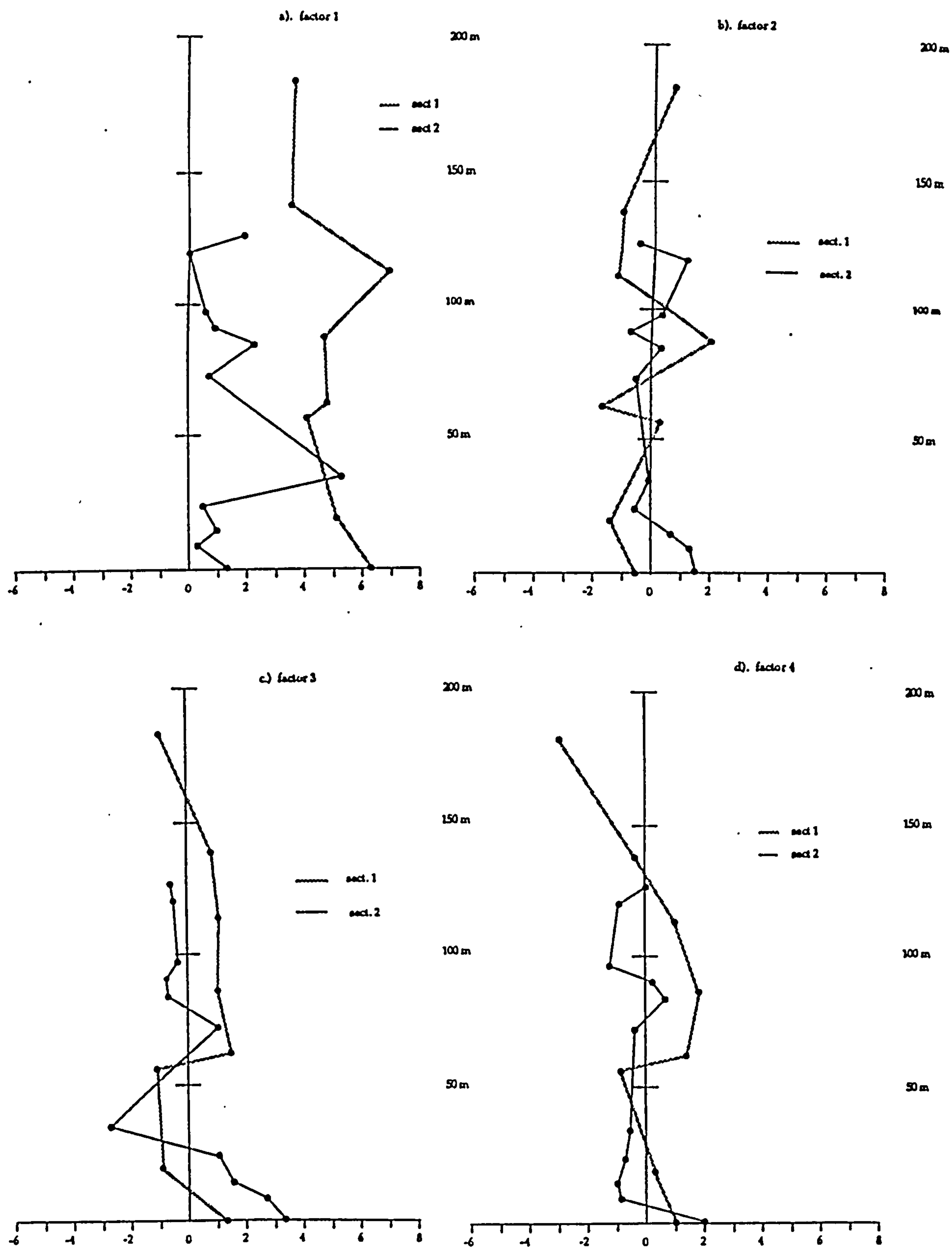


Fig. 5.5.3 Vertical geochemical trends, Straiton Greywacke Conglomerate

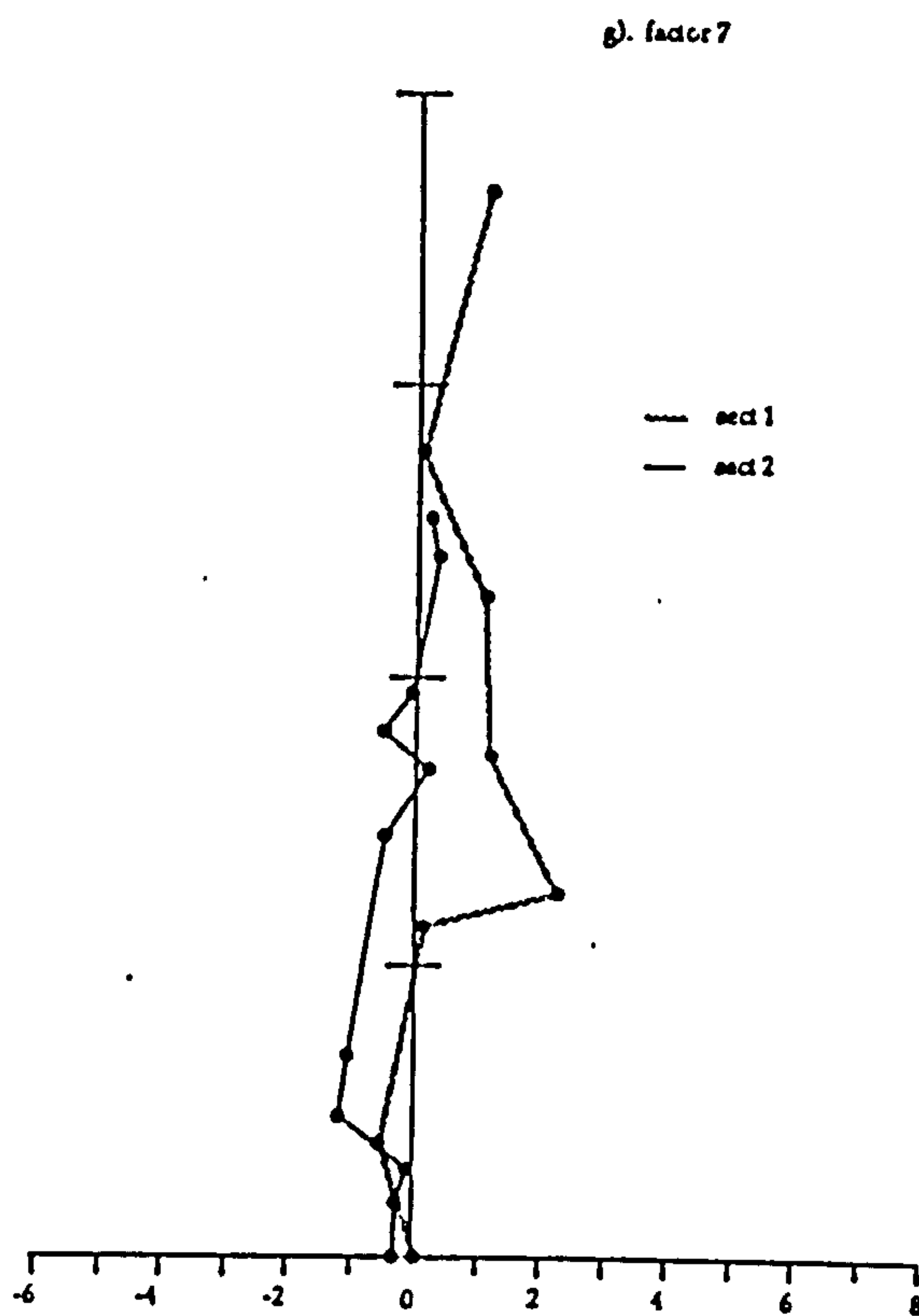
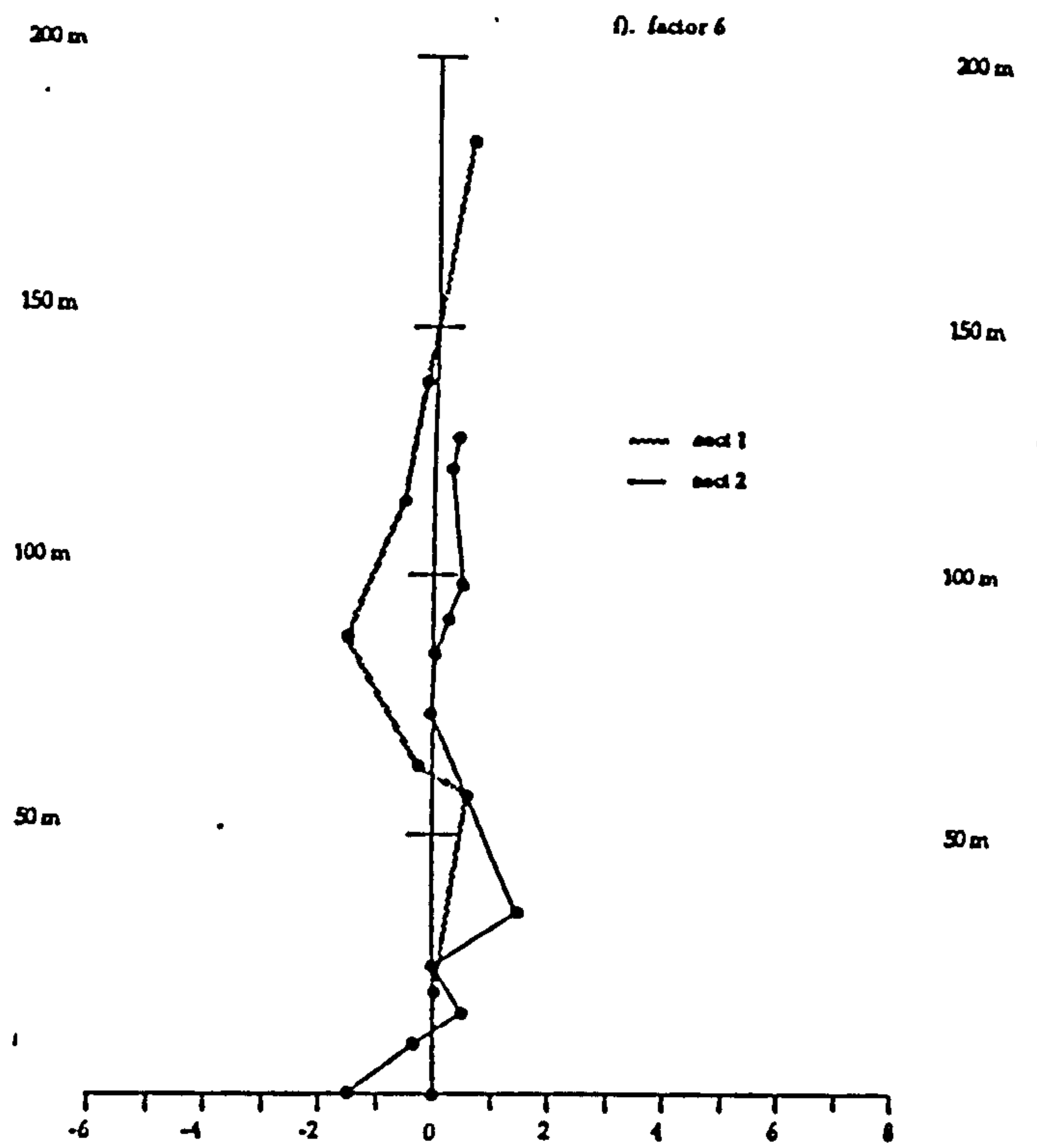
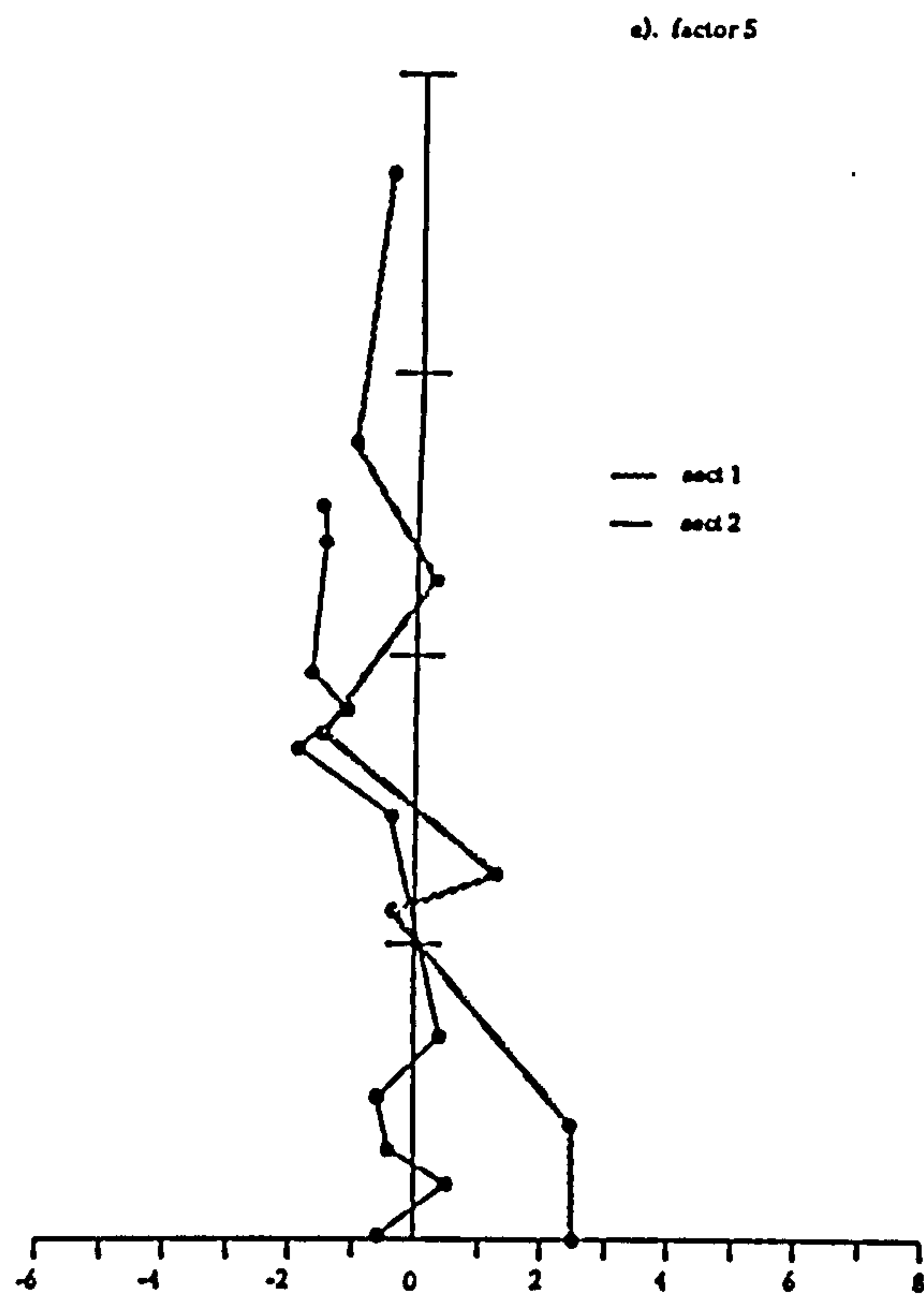


Fig. 5.5.3 cont.

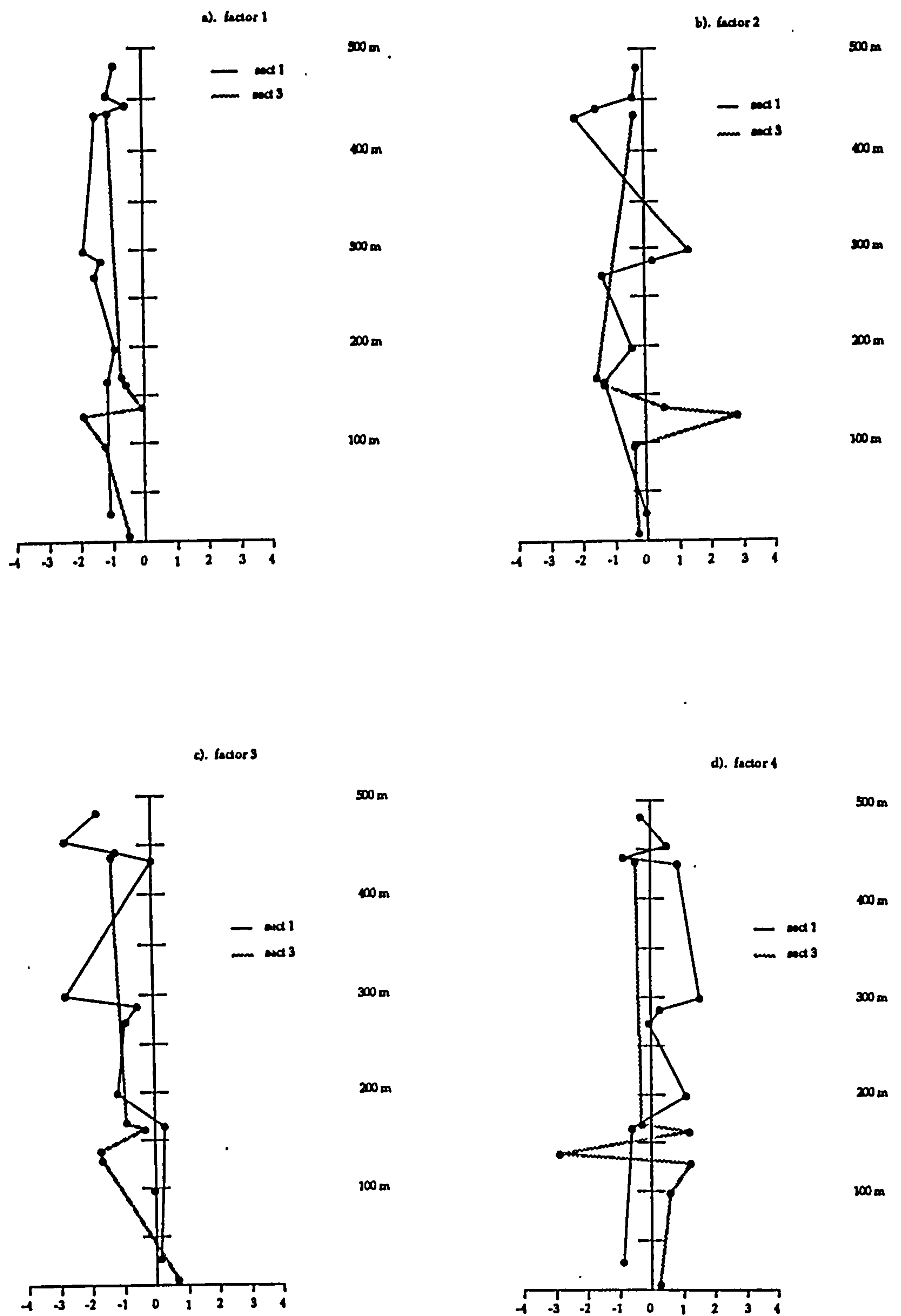


Fig. 5.5.4 Vertical geochemical trends, Hagshaw Hills Greywacke Conglomerate

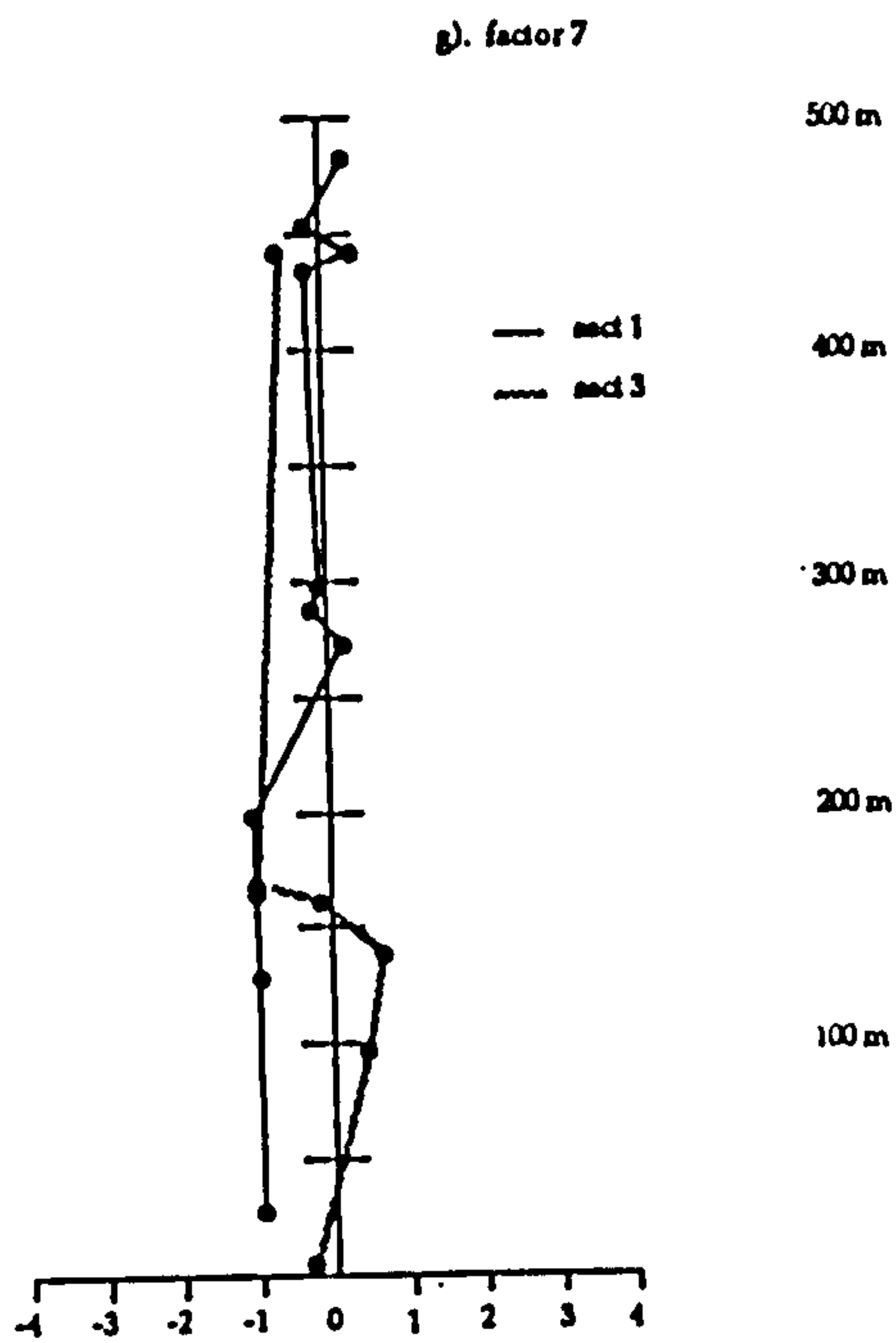
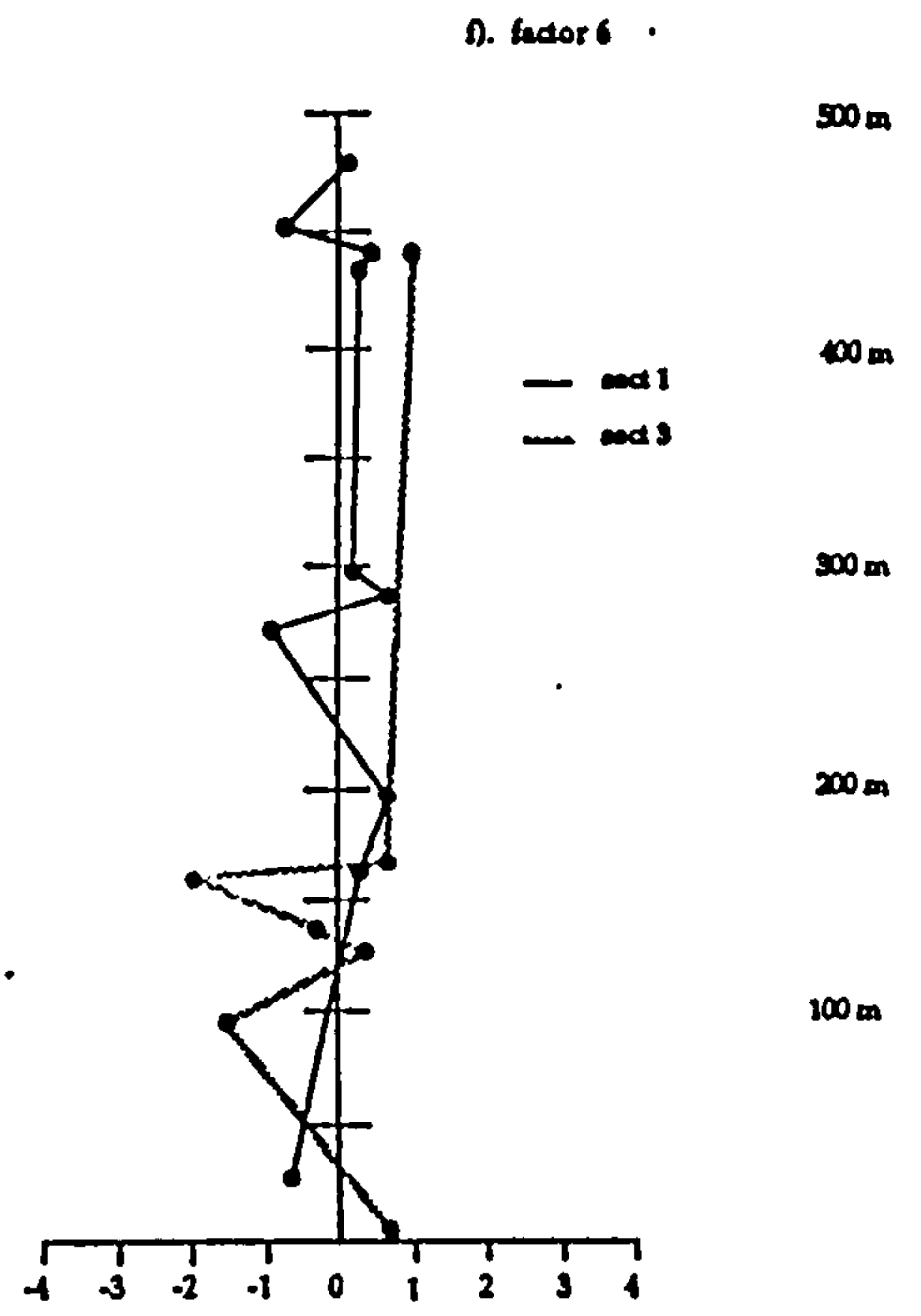
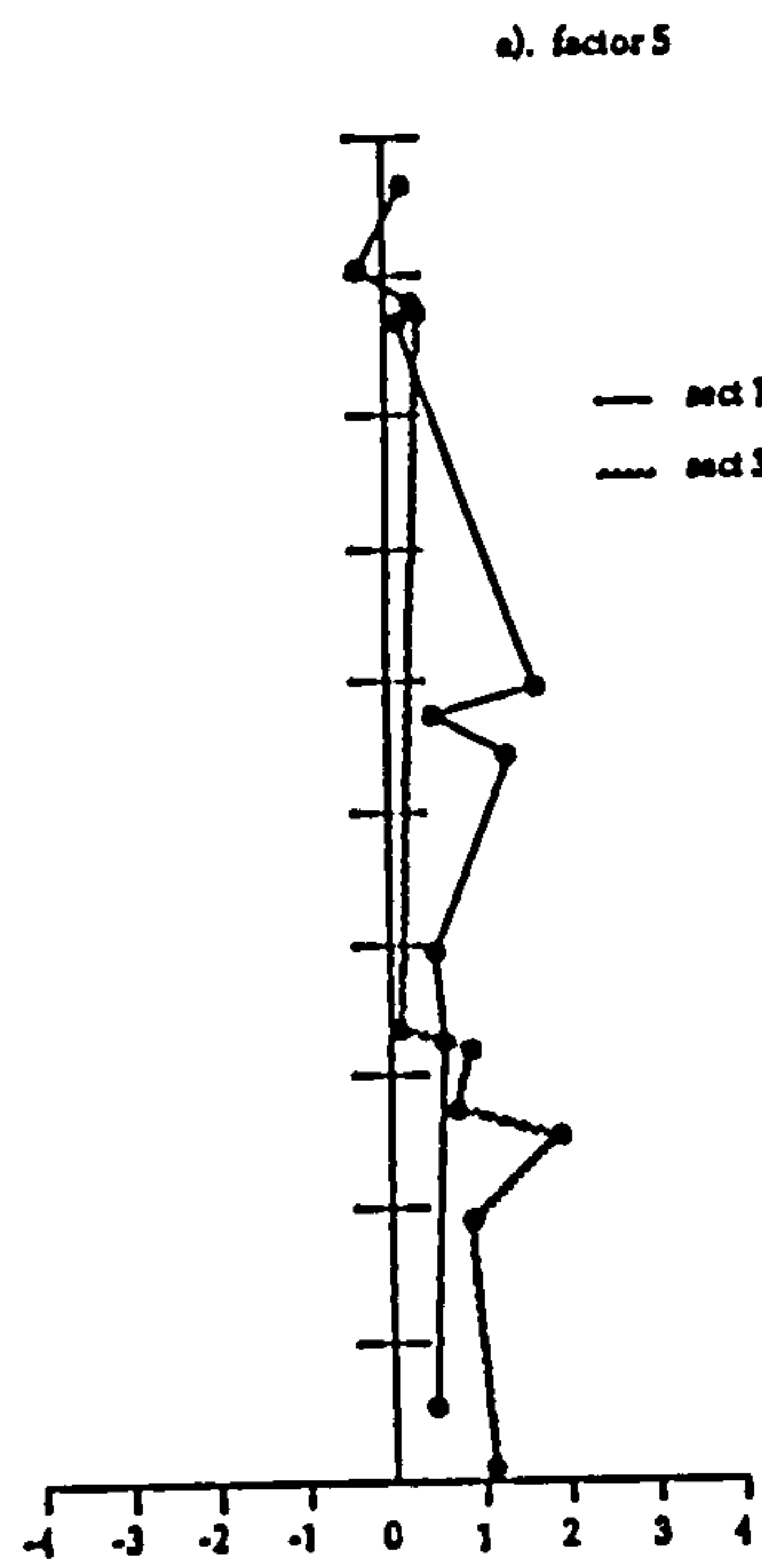


Fig. 5.5.4 cont.

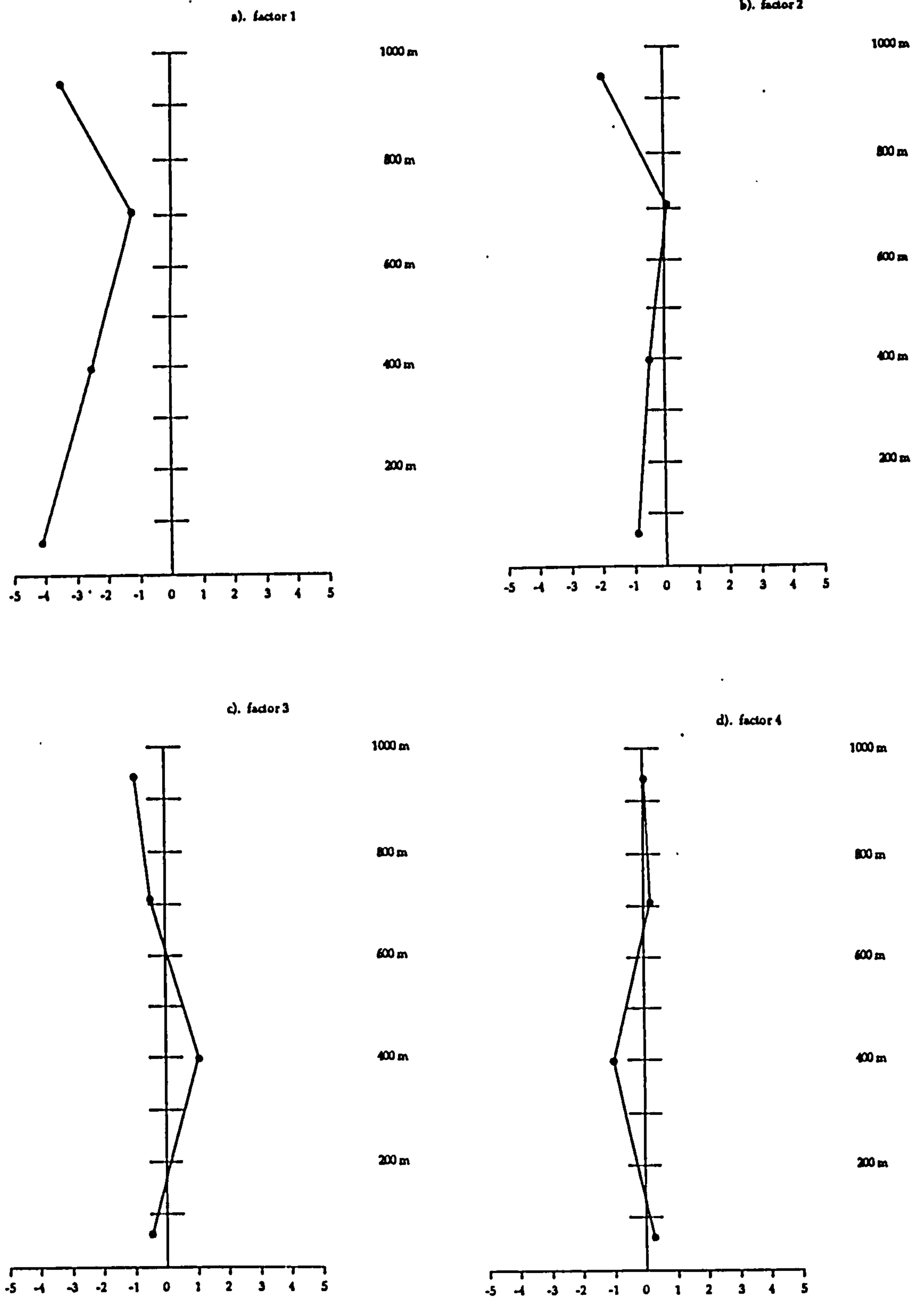


Fig. 5.5.5 Vertical geochemical trends, Tinto Greywacke Conglomerate

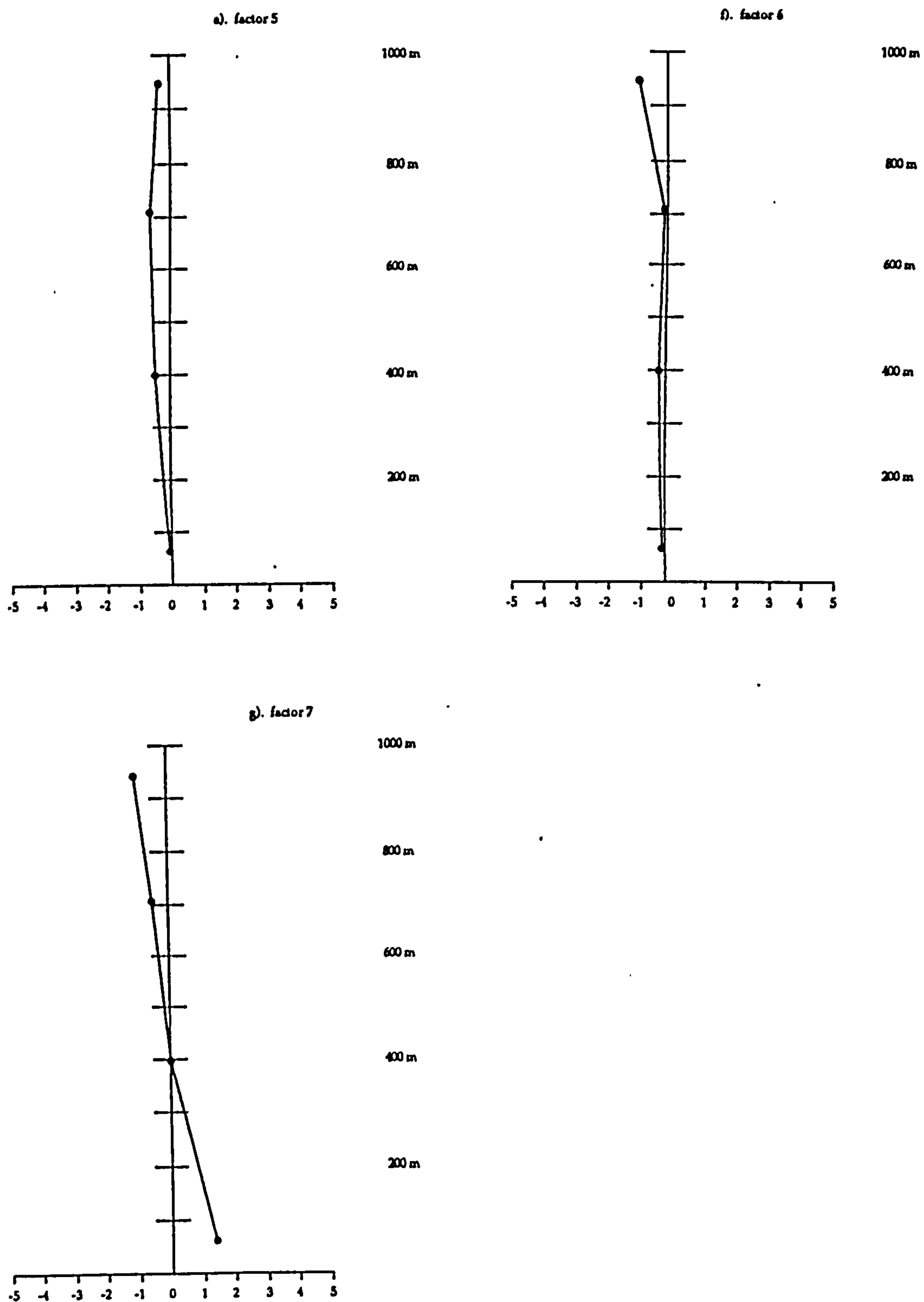


Fig. 5.5.5 cont.

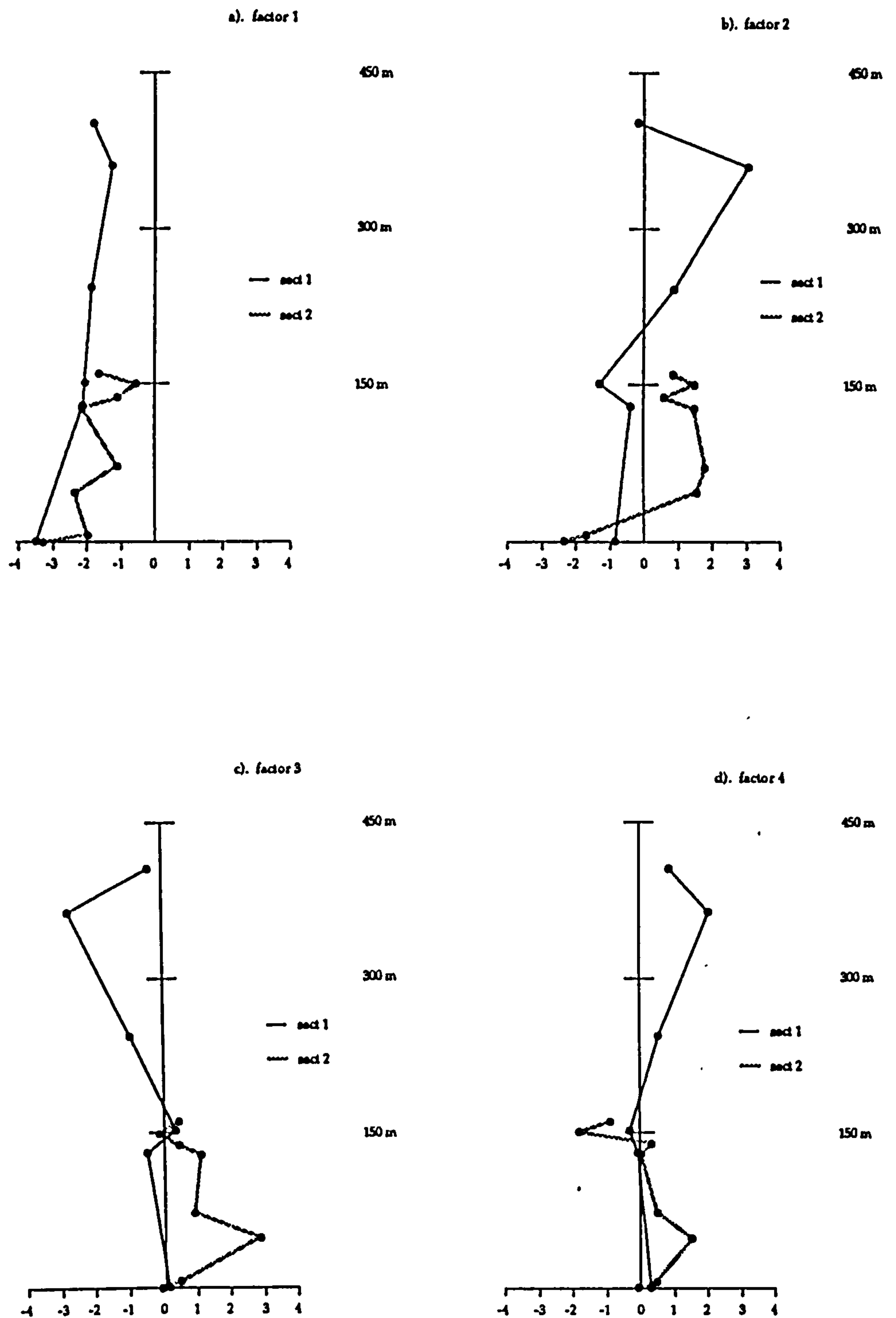


Fig. 5.5.6 Vertical geochemical trends, North Esk Greywacke Conglomerate

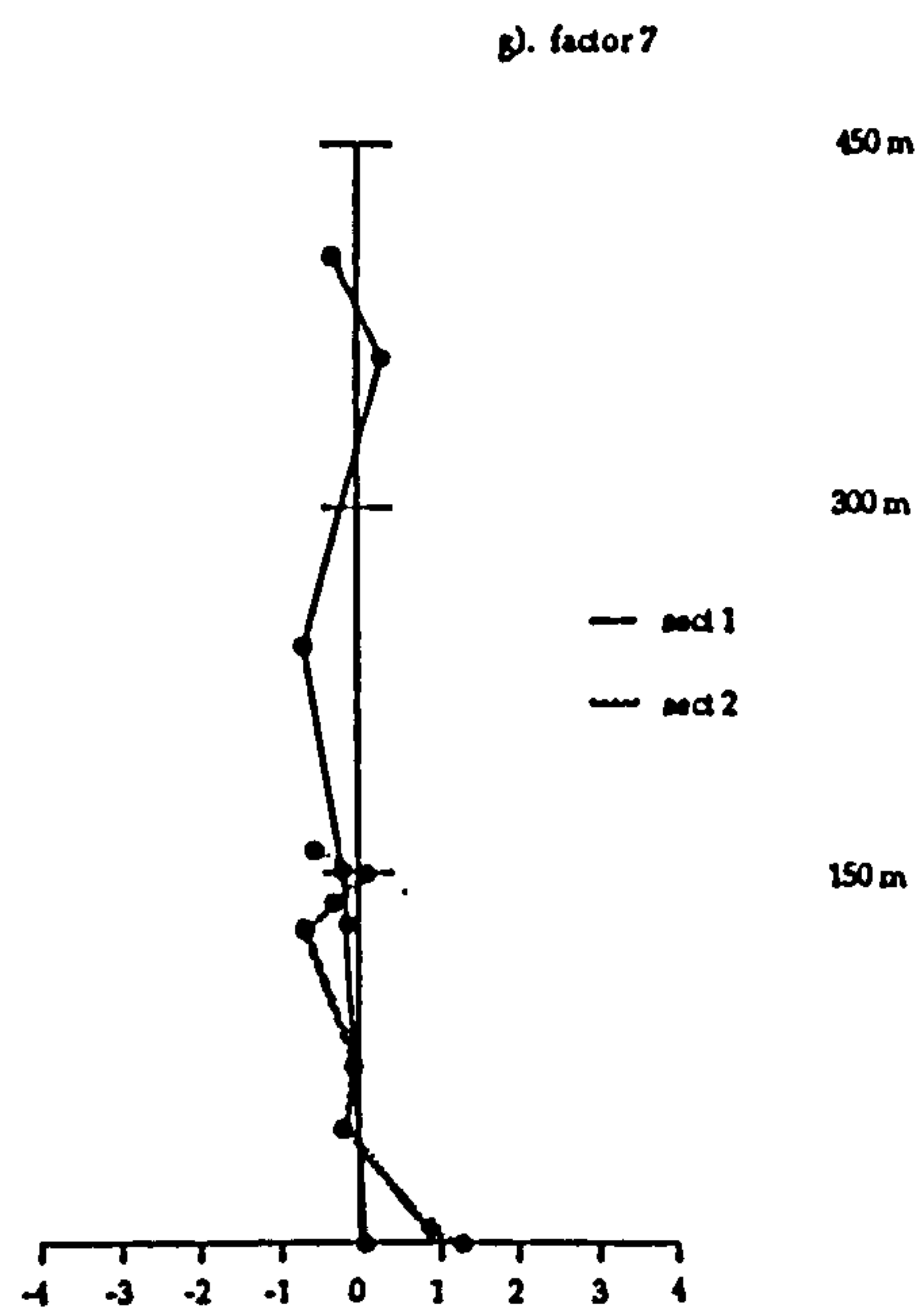
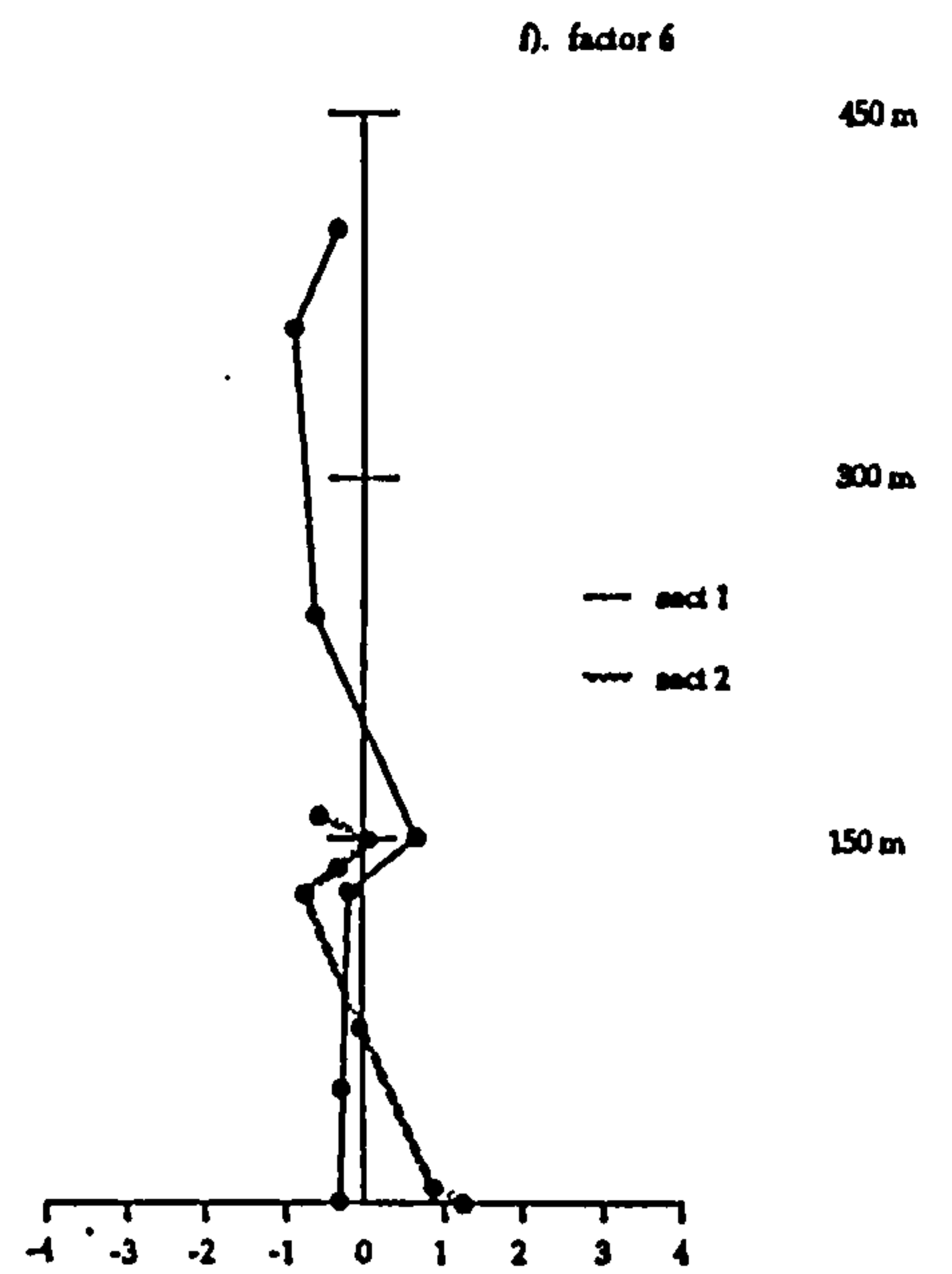
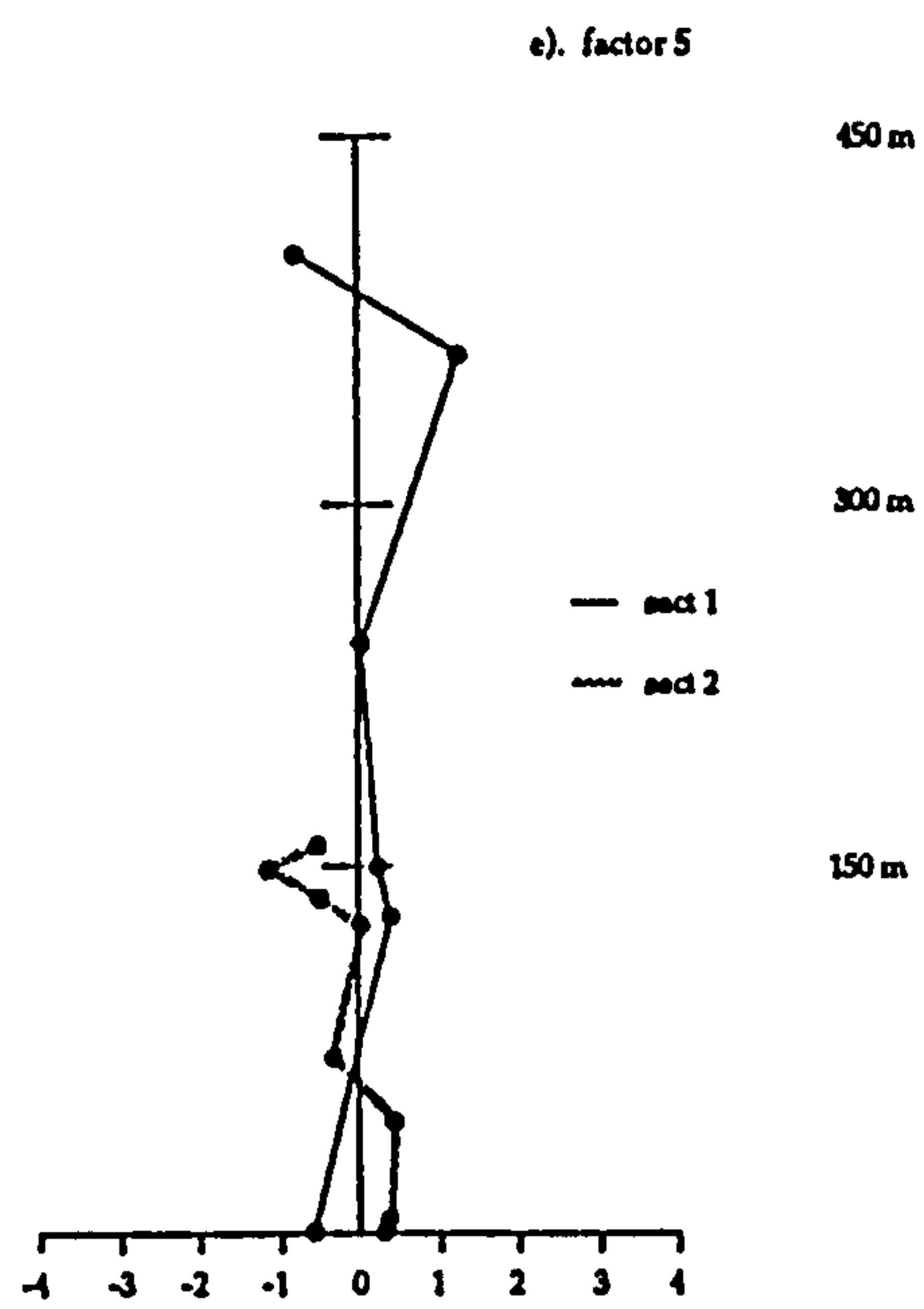


Fig. 5.5.6 cont.

6.0 Tectonic implications of the work studied

The recognition of mineralogical and geochemical differences between the Midland Valley sandstone clasts and Southern Uplands sediments leads to the conclusion that a source for the sandstone clasts other than the Southern Uplands must be sought. Palaeocurrent data suggest that the source region lay to the east or (?)northeast of the Midland Valley and is in direct contrast to present theories of a southerly source. These conclusions pose two questions:

- i). what is the nature and location of the source block
- ii). what is the relationship between the source block, Laurentian margin and Midland Valley basin.

A number of possible models have been investigated to relate the evolution of the Midland Valley to the original source block for the Greywacke Conglomerate.

6.1 The nature of the source block .

The source for the Midland Valley sandstone clasts was a thick pile of flysch sandstones. Mudstone and/or shale clasts are completely absent from the Greywacke Conglomerate, even in the least reworked conglomerates at the top of the section. Despite the fact that shales would break-down very easily and therefore fail to be preserved, it is probable that there was a high sandstone/shale ratio in the original source region. A similar proximal turbiditic source for the Old Red Sandstone Crawton Group sandstone clasts in the northeastern Midland Valley was envisaged by Haughton (1988).

It is important here to make the distinction between the greywacke clasts and the source for the greywacke clasts. The sandstone clasts within the Greywacke Conglomerate preserve a record of the change along the original continental margin where the turbidite assemblage, which was to later become the source for the Greywacke Conglomerate, was initially deposited.

Petrographic and geochemical data shows that the Greywacke Conglomerate records the successive erosion of a turbidite assemblage which ranges from passive-margin (SW) to active tectonic setting sandstones (NE) with progressive enrichment of arc-derived sediment. The Straiton section 1 sandstones are particularly important because they have little or no arc-detritus and are interpreted as the passive margin sediments of the original continental margin. The source along the original continental margin for the passive-margin type sandstones was an actively eroding metamorphic terrane dominated by metaquartzite with little or no input from a plutonic source and only very minor additions of deformed acid-volcanics.

Although, repetition of quartz-rich & quartz-poor sandstones occur within greywacke sequences, *e.g.* the Ordovician Southern Uplands, the thickness and chemical homogeneity of the quartz-rich clasts in the Straiton section 1 indicates erosion through a substantial pile of quartz-rich sandstones and not intermixed units. Therefore, a passive-margin type setting during deposition of the original source which gave rise to the Straiton section 1 clasts is favoured.

The lateral chemical and mineralogical changes in the sandstone clasts from the Straiton through to the North Esk record the spatial and/or temporal changes along the original continental margin. As erosion of the continental margin continued, a sequence of feldspathic quartzites and schists (typical of Straiton section 2) samples were exposed. This metamorphic assemblage continued to be eroded throughout the deposition of the original flysch sediments. Orthoclase-bearing metamorphics typical of the Straiton sandstone clasts give way to increasing plagioclase and volcanic fragments in the Hagshaw Hills samples where the first appearance of a significant amount of mafic-detritus associated with an active destructive margin along the original continental margin is seen. However, in these clasts acid-volcanic fragments are more abundant than basic. The Tinto-Carmichael and North Esk samples show an increase in volcanic detritus and suggest the dissection of a volcanic-arc province which varied from mafic (T-C) to acid (NE) volcanic.

While the increase in orthoclase/na-plagioclase in the North Esk samples has been attributed to more mature volcanic fragments, the high orthoclase content in the Tinto-Carmichael samples is more likely to be associated with a contribution from granitic-plutons. Acid-volcanic fragments in the Hagshaw Hills and granitic detritus in the Tinto-Carmichael sandstone clasts are not indicative of a newly developed volcanic-arc where basaltic-andesitic debris would be anticipated. These acidic-igneous fragments may record erosion through an older and more deeply eroded arc feeding a passive-margin. The most mafic sediments (T-C) in the original flysch basin could be associated with renewed tectonic activity where active subduction was occurring. Alternatively, active subduction may have been at some distance along strike to the basin as suggested by the higher degree of rounding in the basic fragments and relatively low proportions.

Vertical trends within the Greywacke Conglomerate (decreasing upward chemical maturity in both the Straiton sections and increasing upward chemical maturity in the Tinto-Carmichael and North Esk) are consistent with the introduction and ultimate dissection of a volcanic-arc along (or along strike to) the original continental margin. The evidence is for a gradual change from the passive margin sediments in the southwest to the arc-derived sediments in the northeast without rapid changes in the source terrane(s) for the greywacke

sediments, which were the ultimate source for the Greywacke Conglomerate.

The arc-rich sediments lack igneous fractionation trends associated with mafic sediments derived solely from fractionating igneous volcanic or plutonic provinces. This was interpreted as mixing of two distinct source terranes, the continental metamorphics and the volcanic arc, within the basin of deposition. Along destructive margins mixing of continental and arc-derived sediments occur in accretionary prisms, fore-arc basins and back-arc basins (*cf.* Mitchell and Reading, 1986). Modern and ancient sandstones from the above tectonic settings show considerable overlap in petrographic and geochemical signatures (Dickinson, 1982; Maynard *et al.* 1982) and this precludes an unambiguous interpretation of the depositional environment for the turbidite assemblage.

Although the chemical and mineralogical maturity is high in the sandstone clasts and equates with the Silurian Southern Uplands, the petrography of the Southern Uplands greywacke sequences as a whole show consistency along strike whereas the Midland Valley sandstone clasts show variation in the same direction, *i.e.* SW-NE. It is possible to explain the oblique nature of the petrographic variation as preferential selection from tracts within the Southern Uplands, although there are still major mineralogical differences which cannot be reconciled. The Straiton sandstone clasts from section 1 have a high percentage of polycrystalline quartz typical only of the Silurian 'Garnetiferous Group' and its equivalents. In contrast the Tinto, Carmichael, and North Esk clasts, particularly the most mafic clasts, are more comparable to the acid-rich Ordovician sediments, *e.g.* the Shinnel Fm., than to the Silurian sediments. It would thus seem highly improbable that the Straiton sandstones had a source in the Silurian Southern Uplands without also receiving material from the Ordovician (which is the more proximal to the basin) while the most mafic sandstone clasts were sourced solely from the acid-rich Ordovician sediments.

The sources for the greywackes which gave rise to the Midland Valley sandstone clasts and the greywackes in the Southern Uplands are broadly equivalent, in that both are located close to an orogenic metamorphic province with significant input from a volcanic arc. Although the Southern Uplands sediments would be more proximal to an active arc system, the drainage system for the greywackes in the Greywacke Conglomerate was strongly influenced by a continental metamorphic basement. The two greywacke assemblages, the Southern Uplands and the source for the Greywacke Conglomerate, could be geotectonically analagous but different in age.

One point that can be made with regard to the similarity between the Southern Uplands accretionary prism and the original depositional site of the greywackes in the Greywacke Conglomerate is that, the Southern Uplands sediments contain reworked

sedimentary material, e.g. shale and chert fragments, typical of an accretionary prism. Although both these fragments are found in the greywacke clasts in the Midland Valley, the Southern Uplands sediments have a much higher proportion of these fragments (cf. sect. 4.3.2), particularly in the coarser sand size, compared to the Midland Valley clasts. It would therefore be suggested that the original depositional site for the greywackes, which ultimately gave rise to the Greywacke Conglomerate, was a fore-arc or back-arc basin.

A schematic diagram showing the location of the magmatic arc and sequential changes along the continental margin (interpreted from the greywacke clasts) during deposition of the turbidite assemblage is shown in Fig. 6.1.1. In summary, the original turbidite assemblage would be initially deposited along a passive continental margin dominated by quartzite rich metamorphic basement. With time, subduction and closure of this basin developed and uplift and erosion of a highly micaceous schist and gneiss metamorphic complex replaced the quartzite rich continental rocks. Simultaneous erosion from both the metamorphic complex and volcanic arc complex produced the mixed mafic-continental sand deposits typical of a fore-arc basin. It thus appears that while the oldest sediments within the turbidite assemblage are found in the Straiton conglomerates the youngest sediments are found in the North Esk conglomerates.

6.2 Location of the source block during uppermost Silurian-(?)Early Devonian.

Palaeocurrent data, obtained mainly from imbricated clasts, show the source terrane for the Greywacke Conglomerate was located approximately east of the present day exposures. This is the most direct evidence that the source was not the Southern Uplands or at least not in the position of the Southern Uplands today.

Williams and Harper (1988) have suggested a basin configuration oblique to the major Caledonian trend for the Midland Valley Silurian sediments and their correlated Irish equivalents. Their evidence suggests that the basin margin was trending approximately northeast and is compatible with the palaeocurrent data for the uppermost Silurian-(?)Early Devonian Greywacke Conglomerate, although evidence presented here indicates that the trend of the basin margin(s) was more northerly than envisaged by Williams and Harper (*ibid*). Imbrication and facies analysis from the Carmichael Quartzite Conglomerate (mapped as Greywacke Conglomerate) also suggests a source for the Quartzite Conglomerate or its surviving extension to the east-northeast. It therefore seems possible that throughout the Silurian the major uplift was oblique to the Southern Uplands Fault. If this view is accepted then the Igneous and Quartzite Conglomerates may also have been derived from an east-northeast source. The Midland Valley arc-inter-arc (Fig. 6.2.1) theory proposed by

Bluck (1983) would need modification if the majority of the volcanic detritus was not supplied from the sides of the basin but instead within the basin.

Not all of the basins would have a similar configuration. Haughton (1988) has suggested the source for the Old Red Sandstone Crawton Group lithic arenites, which are geochemically indistinguishable from the Hagshaw Hills, Tinto, Carmichael and North Esk sandstone clasts, was from the south-southeast at almost 90° to the uplifted margin for the Greywacke Conglomerate. However, Bluck (pers. comm.) has indicated that the Crawton Group conglomerates may be more easterly dispersed than envisaged by Haughton. The data shows that the source for the Lower Old Red sandstone clasts along the northeastern and the southern margins of the Midland Valley was within the Midland Valley block itself. At present there are no exposures within the Midland Valley which could have supplied the sandstone rich conglomerates seen in the Old Red Sandstone basins. It may be that:

- 1). the Upper Palaeozoic cover obscures the source region
- 2). the source block was subsequently removed by lateral-slip
- 3). the Greywacke Conglomerate records the emplacement of an allochthonous terrane within the Laurentian continent which has been completely removed by erosion.

6.3 Relationship between the source block, Laurentian margin and Midland Valley basin.

Haughton (1988) showed through Sm-Nd isotopic modelling that the original source for the lithic arenite clasts in the Crawton Group could have been the product of mixing a mid-Proterozoic crust with Caledonian age MORB type basaltic material. In contrast, the greywackes of the Southern Uplands are isotopically distinct from the Midland Valley clasts and can be modelled by mixing mid-Proterozoic crust with contemporaneous andesitic-arc detritus. Ophiolitic emplacement along the Laurentian margin was largely accomplished during the Early Ordovician, Tremadoc-Arenig, (Dewey and Shackleton, 1984). The contribution from an ophiolitic source and the enrichment of Ni and Cr (*cf.* Hiscott, 1984), particularly in the metagreywackes associated with the lithic arenites and their association with Ordovician age fossiliferous limestones led Haughton (*ibid*) to consider an Ordovician age for the sandstone clasts. Ni and Cr values in the Greywacke Conglomerate sandstone clasts are similar to the lithic-arenite clasts and are relatively low even compared to the Southern Uplands with no major contribution from an ophiolitic source but a large contribution from an andesitic-arc province. It seems very unlikely that an Ordovician Laurentian continent with obducted ophiolitic sheets could have supplied significant detritus to the original depositional basin for the greywacke source which gave rise to the Greywacke Conglomerate. If it is assumed that the source block is Laurentian in origin, then the absence of mafic detritus in most of the Straiton clasts would indicate these sediments were deposited prior to Ordovician ophiolite obduction and may relate to fore-arc sediments between a

closing basin which pre-dates the Tremadoc-Arenig ophiolite obduction. The age of the turbidite assemblage may ultimately span the Cambrian to earliest Ordovician.

The metamorphic source for these sandstones could have conceivably been the pre-Arenig Midland Valley metamorphic basement. Recent studies (Kelley and Bluck, 1989) have shown that there was a rapidly uplifting metamorphic source in and/or peripheral to the Midland Valley during Ordovician times. However, the majority of the mica-ages are Middle Ordovician, *i.e.* post Ballantrae obduction, and an older metamorphic basement with a high quartz/mica ratio would be assumed to have been exposed prior to ophiolite obduction giving rise to the quartz-rich passive-margin type sandstones.

During the Middle Ordovician the Midland Valley proximal fore-arc near Girvan records the rapid erosion from a coeval volcanic-plutonic arc and the obducted Ballantrae Ophiolite Complex. A considerable amount of granitic and mafic-ultramafic material entered the adjacent basin from the northwest. The most siliceous clasts from the Greywacke Conglomerate unconformably overlies the proximal fore-arc sequence and it is improbable that they represent any equivalent uplifted distal turbidite sequence for the reasons outlined above. The deposition of the original turbidite source for the Greywacke Conglomerate was removed in either distance or time from the middle Ordovician Midland Valley Girvan sequence. Fresh andesitic fragments from the Southern Uplands yielded Lower and Middle Cambrian ages (Kelley and Bluck, 1989) and attest to an earlier volcanic province other than the Ordovician volcanic-plutonic arc at Girvan.

The Midland Valley Silurian conglomerates, the Igneous and Quartzite Conglomerates, contain a sedimentary component similar in hand sample to the sandstone clasts in the Greywacke Conglomerate. Petrographic and geochemical results for the sandstone clasts in the Carmichael conglomerates (which are virtually identical to the Quartzite Conglomerate) are not significantly different from the clasts in the Tinto or North Esk Greywacke Conglomerate. If the sedimentary fraction in the Silurian conglomerates proves to be the same as the Greywacke Conglomerate, as suggested by the above results, then the source for the Greywacke Conglomerate would, in any case, be older than the Wenlock(?) Igneous Conglomerate.

It is interesting that the same constituents and the relative proportions of clasts seen in the Igneous and Quartzite Conglomerates (with the exception of the Girvan succession which has more granitic clasts and derived from a northwesterly source) are also present in the sandstone clasts in the Greywacke Conglomerate, *i.e.* high ratio of acid/basic igneous fragments, abundance of metamorphic fragments and low occurrence of granitic debris. The source for the Greywacke Conglomerate clasts could be distal sediments from the same margin

which gave rise to the Silurian Igneous and Quartzite conglomerates, *i.e.* fore-arc sediments off an acidic arc founded on a metamorphic basement.

In summary, the presence of sandstone clasts similar to those in the Greywacke Conglomerate within the other rocks belonging to the Silurian Midland Valley basins may indicate:

- 1). a rising fore-arc or back-arc basin associated with an active Midland Valley Silurian arc, the culmination of uplift represented by the Greywacke Conglomerate
- 2). the turbidite assemblage sourced from an older acidic arc, is allocthonous to the Silurian Midland Valley and accreted to the Midland Valley before the (?)Wenlock.

The age of the sedimentary succession is of clear importance in deciphering the relationship of the source to the Laurentian margin. Evidence indicates the succession is pre-Wenlock and possibly pre-obduction Ballantrae Complex (Tremadoc-Arenig) and was not derived from the Llandovery age sediments exposed in the Southern Uplands Central Belt.

The proportion of lithic fragments in the Greywacke Conglomerate sandstone clasts (high acidic/basic volcanics, low granitic, and high metamorphic) closely resembles the Wenlock age conglomerates in the Midland Valley and may represent the erosion of an arc and its 'fore-arc' basin. However, the passive-margin type sandstones within the turbidite assemblage are difficult to justify along a pre-Wenlock Silurian Laurentian margin where at least in the Girvan succession there is evidence for an active volcanic-tectonic environment in the Llandovery. If the succession is pre-Silurian then a source on the Laurentian continent prior to ophiolite obduction would be anticipated.

As a final note, during the studies a single fossil (plate 6.1) was found in a sample from the Hagshaw Hills. This fossil is presently being investigated and may be the only available evidence needed to prove the age of the original source for the Greywacke Conglomerate. Holland, C. H. (pers. comm.) has indicated the greywacke succession may be Cambrian in age and this would satisfy the other constraints concerned in this chapter.

6.4 Emplacement of the Greywacke Conglomerate source: within or along the Midland Valley?

The basin fill during the uppermost Silurian in the Midland Valley was dominated from uplifted highlands in the east or northeast with one important exception, the Crawton basin, which was dispersed from highlands in the south. The Crawton basin is particularly important since the lithic arenites (but not necessarily the metagreywackes) are geochemically indistinguishable from the sandstone clasts in the southern Midland Valley

Greywacke Conglomerate (with the exception of the Straiton conglomerates) and therefore may share the same source region. These sandstone clasts in the Old Red Sandstone basins cannot be readily matched to any known source currently exposed in northern Britain.

The sedimentology of the Greywacke Conglomerate suggests that a series of small vertically stacked alluvial fans occurred adjacent to N-S trending marginal faults. The dominance of proximal sediment-laden sheet flood deposits upward through the sections indicates basin subsidence was rapid and exceeded uplift throughout much of the deposition. Renewed fault activity within the basins continued to be an important mechanism until the final stages of deposition where first cycle clasts in proximal or mid-fan braid plain deposits are seen in the Straiton conglomerates. The very end stages of sedimentation also changed radically where pebbly sandstones succeed proximal alluvial deposits. The dominant westerly direction of transport indicates that the Greywacke Conglomerate was laid down in a series of en echelon basins with the major uplift along the eastern block. The evidence that these basins were separated comes mainly from the fact that they were filled by small fans probably not exceeding 2 km in length suggesting local sources. Each basin is dominated by proximal fan deposits recording the progressive erosion through a 'fore-arc' sequence. There are three possible models which might explain these facts concerning the Silurian basins.

6.4.1 Model 1: Deposition along the Midland Valley Laurentian margin by passing fore-arc slivers.

If the argument that subduction continued until after deposition of the Greywacke Conglomerate is accepted then the opening of rapidly subsiding basins oblique to the major Caledonian trend needs to be addressed in a model which relates closure of an oceanic basin to extensional tectonics. A number of authors have suggested that the closure of the Iapetus Ocean resulted in transportation of a number of exotic terranes by sinistral slip along the Laurentian margin (*cf.* sect 1.2). Jarrard (1986) has recently pointed out that arc-parallel strike-slip faulting occurs behind 50% of modern subduction zones and prolonged periods of oblique subduction can result in terrane migration of fore-arc slivers. The occurrence of a 'fore-arc' sedimentary sequence in the Silurian Midland Valley conglomerates which cannot be easily matched to a known province may have been generated in a similar manner. The Greywacke Conglomerate may record the main erosional event of a passing fore-arc terrane as suggested by Haughton (1988).

One model which could accommodate both strike-slip terrane accretion and half graben basin formation oblique to the principal displacement zone is the opening of a series of pull-apart basins along a releasing fault overstep (Harding, *et al.* 1985) or divergent bend in the main fault. The basins need not have formed in their present position but instead could have been transported along an active lateral fault resulting in an exotic strike-slip duplex, a

system of steep imbricate faults which merge into the major strike-slip fault (Woodcock and Fischer, 1986, Fig. 9). In this model the basin(s) are formed adjacent to their source terrane along a fault bend, all the displacement is then taken up on one of the bounding faults, continual displacement removes the duplex from one wall and finally a switch in the active fault to the opposite margin and continual displacement removes the basin duplex from the remaining attached wall (Fig. 6.4.1 a-c). The deposition of exotic clasts from fore-arc slivers into basins, each with a unique petrography would necessitate the fore-arc terrane to be already deformed and in a vertical position before movement along the principal displacement zone commenced. The eventual removal of the initial source fore-arc blocks similar to the method described above would leave a series of basins recording the passing of the terranes along the Midland Valley Laurentian margin. A closer look at ancient and modern extensional strike-slip basins will prove beneficial in assessing the likelihood that the Greywacke Conglomerate was deposited in a strike-slip setting.

Nilsen *et al.* (1985) in a comparison of three basins, the Hornelen Basin in western Norway and the Ridge and Sulphur Creek Basins in California which have been used for models in strike-slip extensional basins, listed a number of similar features which can be used for comparison to the Midland Valley Greywacke Conglomerate. In each case the basins were filled axially along the length but more importantly from more than one marginal fault. Along the marginal faults, which include conjugate splays off the major displacement zone, the principal strike-slip fault showed the greatest amount of vertical displacement with small (≤ 2 km) alluvial debris-flow dominated fans along the margin. In some extensional basins formed by strike-slip tectonics the steepest slopes are not associated with the principal displacement zone but along high-angle normal faults (splays) which either terminate or merge into the strike-slip zones, *e.g.* the Walker Lake Basin, Nevada, Link *et al.* (1985).

The most important sedimentological control common to all these basins is that they are bounded by more than one marginal fault, one the master strike-slip fault, which dispersed sediment into the basin. Although only one lateral fault may be active at any one time, both it and its conjugate splays will control sedimentation and disperse sediment into the basin from at least two margins. The sedimentation of the Greywacke Conglomerate does not suggest deposition from more than one marginal fault, specifically dispersal from the principal displacement zone, the Southern Uplands Fault or its NE-SW trending ancestor.

The geometry of the fault system can also lead to some important considerations. If a major strike-slip displacement zone existed in the southern Midland Valley in the Lower Palaeozoic with the same orientation as the Southern Uplands Fault then both the Riedel, P shears and tension fractures would be at too low an angle, *e.g.* set of NE-SW trending faults

(strike similar to Great Glen) in Grampian highlands are considered to be first order Reidel shears off the Highland Boundary Fault Zone (Soper, 1986), and the conjugate Riedel shears would be over-rotated to have formed the dominate N-S basin(s) margin. However, the orientation of faults in real geological settings do not necessarily conform to predicted models in simple ideal systems (Christie-Blick and Biddle, 1985) but for a Caledonian trending NE-SW fault a first approximation does not reveal N-S trending uplifted margins characteristic of the Greywacke Conglomerate. The passing of an exotic terrane only along the northern margin of the basins would not generate rapidly subsiding basins south of the displacement zone.

6.4.2 Model 2: Deposition of the Greywacke Conglomerate from advancing thrust sheets.

McClay *et al.* (1986) have suggested that Old Red Sandstone deposition in the northern and central British and Scandinavian Caledonides is analogous to the Basin and Range province in the western United States where relaxation of an overthickened crust related to compressional tectonics resulted in reactivation of previous thrust sheets as extensional faults. The authors view the Midland Valley basin as an extensional basin formed along the southern boundary of an overthickened Caledonian thrust. This hypothesis supports a thickened Caledonian crust during deposition of the Old Red Sandstone whereas erosion of the Dalradian occurred prior to deposition of the Old Red Sandstone in the Midland Valley (*cf.* sect.1.1). The recognition of the Great Conglomerate in the Southern Uplands as Old Red Sandstone in age with similar sandstone clasts to the Greywacke Conglomerate indicates that the Southern Uplands block was receiving and not supplying sediment during this time. It is therefore probable that the Southern Uplands also had a depositional surface which was probably relatively flat lying during Old Red Sandstone times.

Although the basal Old Red Sandstone Greywacke Conglomerate was deposited in rapidly subsiding basins, the controlling marginal faults were within the Midland Valley and not related to collapse of the NE-SW trending Southern Uplands Fault or Highland boundary Fault. E-W convergence between Laurentia and Baltica during the mid-late Silurian (Soper, 1986; Soper and Hutton, 1984) produced the opposing thrust system in Northern Britain and Scandinavia, *e.g.* the Moine thrust. It is possible that thrust systems were produced in the Midland Valley or to the ENE in the present day North Sea and have now been completely eroded.

The deposition of the Greywacke Conglomerate and Old Red Sandstone basin formation in the southern Midland Valley could therefore be related to either:

- i). a foreland basin along an advancing thrust sheet or

ii). extensional relaxation of existing Midland Valley basement possibly related to mid-late Silurian continental collision of Baltica and Laurentia.

The model for the deposition of the Greywacke Conglomerate including the Igneous and Quartzite Conglomerates within a foreland basin is shown in Fig. (6.4.2 a). In this model the source for the Greywacke Conglomerate and possibly the Igneous and Quartzite Conglomerates would be located in the rising nappe. The erosional model of a foreland thrust suggested by Graham *et al.* (1986) has some similarities to the overall stratigraphical succession and clast composition in the Silurian Midland Valley but cannot adequately account for the sedimentological characteristics of the conglomerates. The Igneous Conglomerate thins and fines toward the WSW and suggests a static foreland thrust offshore to the ENE of the Midland Valley where subsidence and sedimentation is greatest adjacent to the advancing thrust sheet (Allen *et al.* 1986). However, in the North Esk inlier the Quartzite Conglomerate is only 2 m thick whereas in the more southwesterly inliers the conglomerate is well developed and cannot be easily explained by the static foreland thrust model.

A static foreland basin margin offshore to the ENE of the Midland Valley is also difficult to reconcile with the proximal nature and consistent grain size of the Greywacke Conglomerate in each of the locality areas along the length of the Midland Valley. The migration of advancing thrust sheets towards the foreland basin with time would generate proximal deposits along the axis of the Midland Valley but would also uplift and rework previous deposits of Igneous, Quartzite and Greywacke Conglomerates (Fig. 6.4.2 b). In contrast, the Greywacke Conglomerate is devoid of acid-igneous clasts and the only occurrence of the quartzite clasts is at the base of the conglomerate. The continual reworking of uplifted basins is characteristic of foreland basins (Reading and Mitchell, 1986) and if a foreland thrust consisted solely of a sequence of greywackes deposited onto pre-existing Silurian conglomerates the model could still not account for the unique sandstone petrography and chemistry within each basin.

6.4.3 Model 3: The greywacke basement model.

The deposition of the Greywacke Conglomerate into locally filled basins suggests the best model would be a pre-existing basement or basement cover of greywacke within the Midland Valley. Two alternative views for greywacke basement in the Midland Valley can be put forth:

- 1). a thick cover of Silurian age greywacke that is autochthonous within the Midland Valley block or

2). the greywacke source was accreted to the Midland Valley Laurentian margin. However, accretion must have taken place before the Wenlock, the age of the Igneous Conglomerate which contains a fraction of the sedimentary clasts. These accreted terranes would thus probably still be present beneath the Upper Palaeozoic cover.

The main objection to a thick cover of autochthonous greywacke over the Midland Valley is the absence of significant amounts of mafic detritus in the sandstone clasts. This would argue for a Silurian age succession, at least for the active-tectonic type sandstones in the greywacke succession but not the passive margin type sandstones. The Llandovery turbiditic sequence in Girvan was itself deposited in a small localized basin (*cf.* sect. 2.1.1) and may be representative of the Midland Valley Lower Silurian as a whole where evidence for localized subsidence is also seen in the Galway Silurian inlier (Williams and Harper, 1988). This would argue against a source in the Midland Valley Llandovery where uplift of these basins would remove a substantial portion of the sequences.

The favoured model would thus be pre-Wenlock accretion of greywacke basement within the Midland Valley block. Uplift and erosion of a pre-existing accreted greywacke basement would generate deposition of the Greywacke Conglomerate in Lower Old Red Sandstone times.

If the theory that the passive-margin sandstones represent the oldest sediments in the source block is accepted, then uplift of a thick undeformed greywacke basement cover would probably never erode deep enough to expose these sediments. Therefore to account for the unique chemistry and petrography of the greywacke clasts in each of the sedimentary basins, the Midland Valley greywacke basement would need to be a package of dipping or vertical strata before uplift and deposition of the Greywacke Conglomerate.

Vertically upward through the Greywacke Conglomerate, the clast composition in each basin shows increasing similarities to the sedimentary clasts in the adjacent ENE basin. This evidence indicates erosion through a gradational package of greywacke that is trending oblique to the main Caledonian NE-SW trend with the oldest sediments in the southwest and the youngest sediments in the northeast (Fig. 6.4.3 a).

The proposed model is obduction of a package of passive margin to 'fore-arc' sediments deposited off the Midland Valley Laurentian margin prior to obduction of the Ballantrae Ophiolite (see Fig. 6.2.1). The Ballantrae Complex could have formed the oceanic floor on which these sediments accumulated and was obducted along with the greywacke basement. The greywacke basement and Ballantrae would be thus accreted and thrust onto the Midland

Valley metamorphic basement along a west-northwesterly direction (Fig. 6.4.3 b). However, the Ballantrae ophiolite is considered to be obducted along a northwesterly direction by Caledonian orthogonal collision. This direction can not account for the oblique petrographic trend seen in the greywacke clasts and an alternative view is the greywacke sequence was accreted to the Midland Valley not during but prior to the Ballantrae Ophiolite Complex (Fig. 6.4.3 c). The accreted greywacke would form part of the Midland Valley basement on which the later NE-SW main Caledonian trend was superimposed.

The accreted greywacke basement would have formed highs since deposition of the Igneous Conglomerate and possibly the Llandovery succession (Fig. 6.4.4 a). It is also possible that during marine conditions colonization of the 'greywacke basement islands' by reef communities took place giving rise to the sporadic occurrence of shelly clasts found in the Hagshaw Hills Igneous Conglomerate.

The Llandovery turbidites in the Midland Valley may be derived from the Southern Uplands emergent trench slope-break as suggested by Mckerrow *et al.* (1977) but there is also evidence to suggest that some of these deposits were dispersed from an ENE source (Mykura and Smith, 1962). A re-appraisal of the directional features associated with the Llandovery up to the Greywacke Conglomerate is needed but a significant proportion of the sediments in the Silurian Midland Valley is dispersed from the ENE-NNE and thus may not be related to plate interaction along the Solway Line, *i.e.* northward or oblique closure of the Iapetus Ocean.

The sedimentological characteristics also indicate the Igneous Conglomerate may also have a source to the east or northeast. The acid-igneous clasts in the conglomerate could be derived from contemporaneous igneous activity as suggested by Bluck (1983), see Fig. 6.2.1, but the volcanicity again may not be related to closure along the Solway Line. Instead, plate interaction along E-W convergence is an alternative model. The Igneous Conglomerate fines dramatically from the North Esk inlier (NE) to the Hagshaw Hills inlier (SW) and any contemporaneous igneous activity during the (?)Wenlock would presumably have been in the ENE Midland Valley (Fig. 6.4.4 b). The roots of the volcanic cones may have later been exposed to give rise to the clasts of granodiorite and tonalite found in the northeastern Midland Valley Old Red Sandstone Crawton basin. Wenlock and Early Ludlow Rb-Sr dates have been determined for the granite clasts and may represent emplacement ages (Haughton, 1986), the approximate age of the Igneous Conglomerate.

In contrast to the Igneous Conglomerate, the Quartzite Conglomerate shows no significant decrease in grain size along strike in the Midland Valley where McGiven (1967) suggested a northwest dispersal. The source for the polycyclic quartzite clasts is unknown and

could have been dispersed from the southeast off a passing migrant terrane and deposited over the greywacke basement highs in discontinuous beds.

A variation in thickness of the Quartzite Conglomerate over the greywacke basement can explain both the persistence of deposition of the Quartzite Conglomerate in the Carmichael area during LORS times (deposition of the Greywacke Conglomerate) and quartzite enrichment at the base of the Greywacke Conglomerate, without any change in palaeoflow direction (Fig. 6.4.4 c). The Midland Valley Silurian Quartzite Conglomerate basins would still show dispersal from the southeast (where possibly deposited by passing terranes) whereas the LORS basins would uplift and rework a discontinuous cover of Quartzite Conglomerate.

Activation or reactivation of a series of N-S trending ~~border~~ faults within the Midland Valley generated a series of rapidly subsiding basins adjacent to major uplifts of the greywacke basement during the uppermost Silurian-(?)Early Devonian culminating in the deposition of the Greywacke Conglomerate (Fig. 6.4.4 d). The most easterly uplifted block identified would be present offshore to the east of the North Esk inlier (see Fig. 6.4.4 a). If the theory that the Southern Uplands has been thrust over the Midland Valley is accepted (*cf.* sect 2.3) then a part of the Midland Valley greywacke basement would have extended at least as far south as the present day Silurian Southern Uplands where the Great Conglomerate accumulated.

It has been argued that the present day Southern Uplands could not have controlled sedimentation during the deposition of the Greywacke Conglomerate and the basin margins could not represent splays off that fault. However, the abrupt truncation of the Greywacke Conglomerate by the Southern Uplands Fault indicates that the whole of the southern Midland Valley LORS basins may not now be present within the Midland Valley. There is a possibility that the Greywacke Conglomerate basin margins are conjugate splays off a strike-slip fault zone but the southern margins (the principal displacement zone) which would show a northerly dispersal are now underneath the Southern Uplands or have been laterally removed. The evidence is therefore compatible with both extensional relaxation of the Midland Valley crust and sinistral slip along a more southerly fault than the Southern Uplands Fault.

There are two possible explanations for the sudden decrease in size of the fluvial system at the top of the Greywacke Conglomerate (the abrupt change from coarse proximal conglomerates to pebble conglomerates which rapidly grade into the overlying sandstones).

- 1). a basin wide (the length of the Midland Valley) abrupt shift to a new location in a fault system or

2). back faulting and diachronous opening of basins by strike-slip tectonics.

A basin wide shift from one fault to another in a strike-slip setting would generally produce and erode new source terranes accompanied by a shift in palaeoflow. Neither of these features are present in the Greywacke Conglomerate. The most likely explanation is a system of back faulting during deposition of the Greywacke Conglomerate. This type of diachronous faulting has been cited by numerous authors in strike-slip tectonic settings in which the progressive opening of basins is antithetic to the palaeoflow (Bluck, 1980c; Steel and Gloppen; 1980, Nilsen and McLaughlin, 1985). However, the evidence is equivocal for the migration of depocentres in the Greywacke Conglomerate. The Straiton section 2 conglomerates are of mixed clast types including clasts typical of Straiton section 1 and the Hagshaw Hills and would suggest faulting in the direction of palaeoflow and not in the opposing direction. Clearly the rapid upward decrease in the fluvial system without major changes in palaeoflow and increasing upward clast similarity in each basin to the adjacent ENE basin is consistent with migration of depocenters in the direction of palaeoflow. However, the vertical upward increase in clast similarity to the adjacent basins is more likely to reflect the petrographic gradational change in the greywacke basement source terrane and perpendicular or oblique erosion through the block. There is also no evidence for increasing fan size in the direction of palaeoflow caused by back faulting and expansion of basin size.

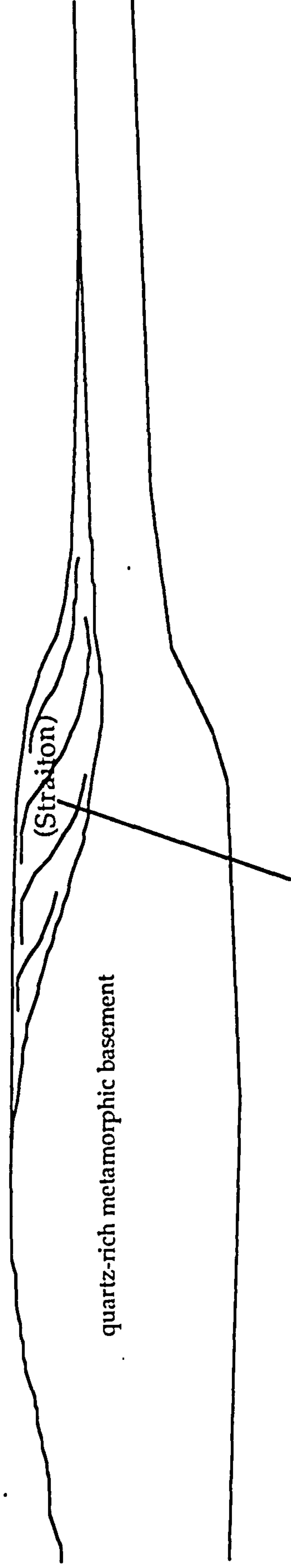
6.5 Wider tectonic implications.

The structural evolution of the southern Midland Valley Old Red Sandstone basins is not well understood and is consistent with both an end-Caledonian E-W extensional cratonic evolution and sinistral-slip along the Midland Valley Laurentian margin. What is important is that they cannot be related to end Silurian strike-slip movement along the present Southern Uplands Fault and control by a more southerly fault (possibly beneath the Southern Uplands) is more consistent with the data. The Greywacke Conglomerate cannot be used as evidence for the time of emplacement of the Southern Uplands (or specific units within the block) against or over the Midland Valley. Accordingly, there is no strong evidence for plate interaction sedimentological control along the Solway Line in the southern Midland Valley from the Upper Llandovery upwards.

The calc-alkaline sequence of Lower Old Red Sandstone lavas which interfinger but mostly overlie the Greywacke Conglomerate could also be more easily related to E-W plate interaction than along the Solway Line. Thirlwall (1981) himself suggested westward subduction beneath the Midland Valley during the Silurian to account for the chemical variation in the lavas. Accordingly, the age of the Greywacke Conglomerate, which must be very close to 410 Ma., indicates the lavas are not Silurian in age but are mostly Early

Devonian and probably post-date continental collision between Laurentia and Baltica (?) and northward subduction beneath Scotland. Therefore, the lavas may represent volcanic activity within the Lurasian supercontinent as suggested by McClay, *et al.* (1986).

a). Passive margin



b). Closing Ocean

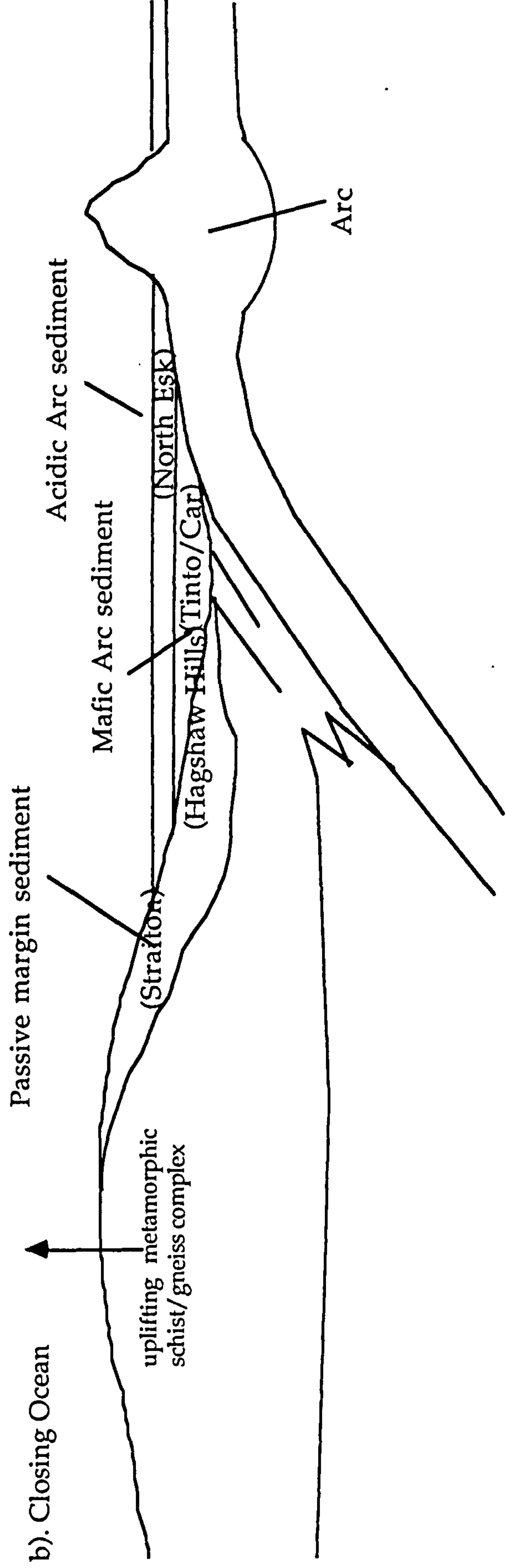
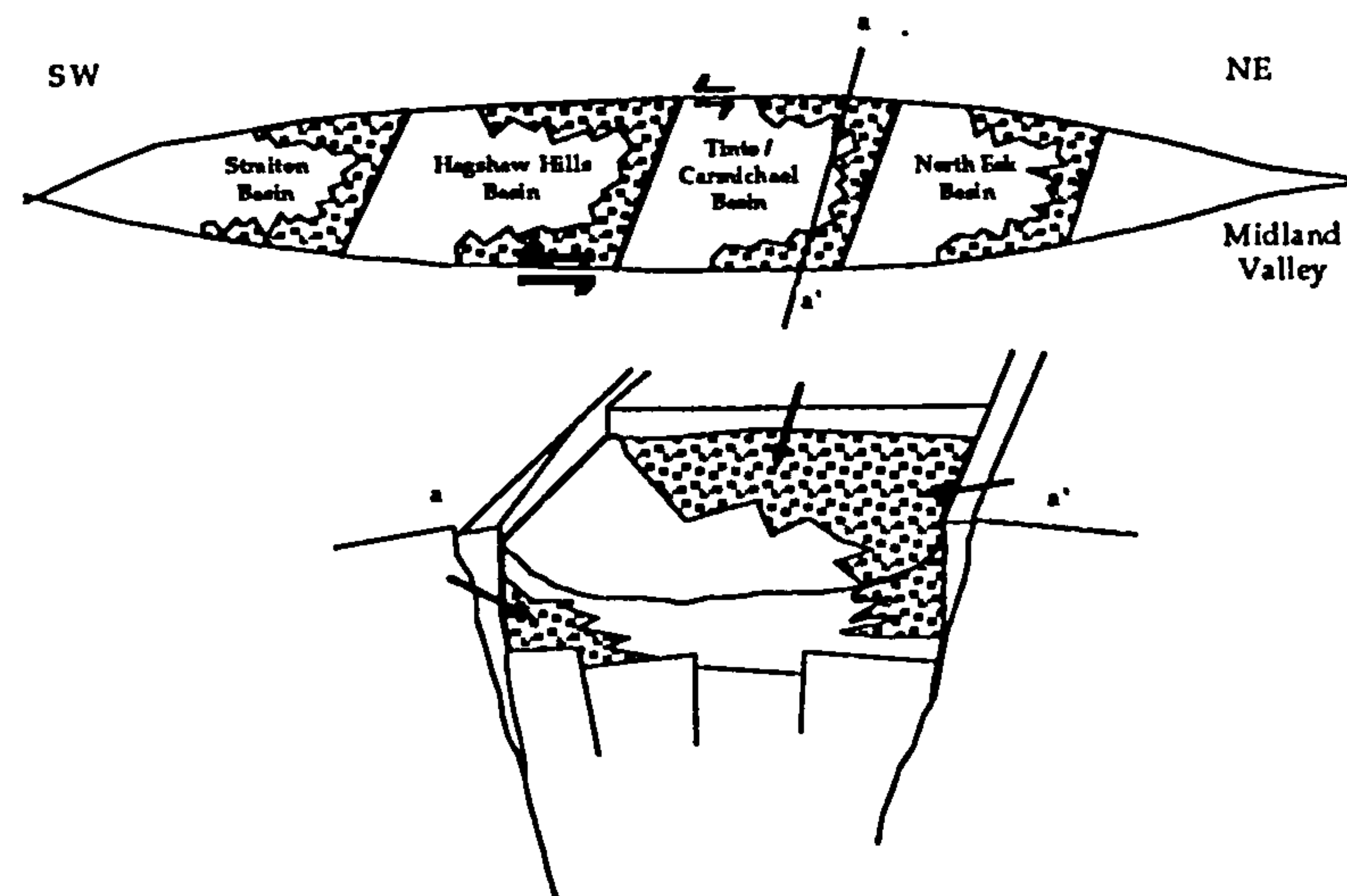
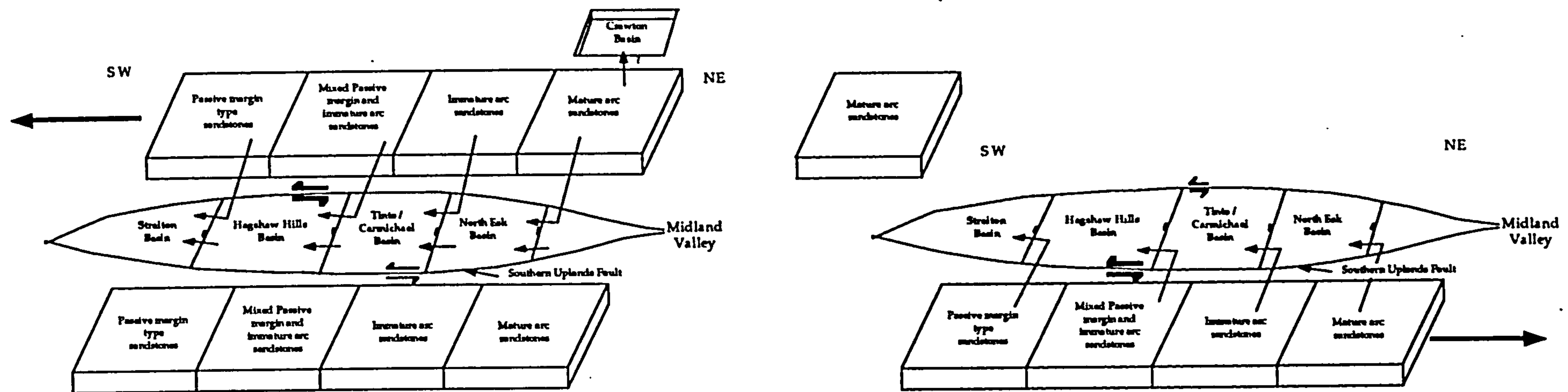


Fig. 6.1.1 Relative tectonic settings of original greywacke turbidite assemblage (later uplifted to become source for Greywacke Conglomerate).



Model 1: Deposition by passing fore-arc slivers

c). Coarse clastic fill of basin from more than one marginal fault.

Fig. 6.4.1 Model 1: Deposition of Grewacke Conglomerate by passing fore-arc slivers

Modified after Woodcock & Fisher (1986)

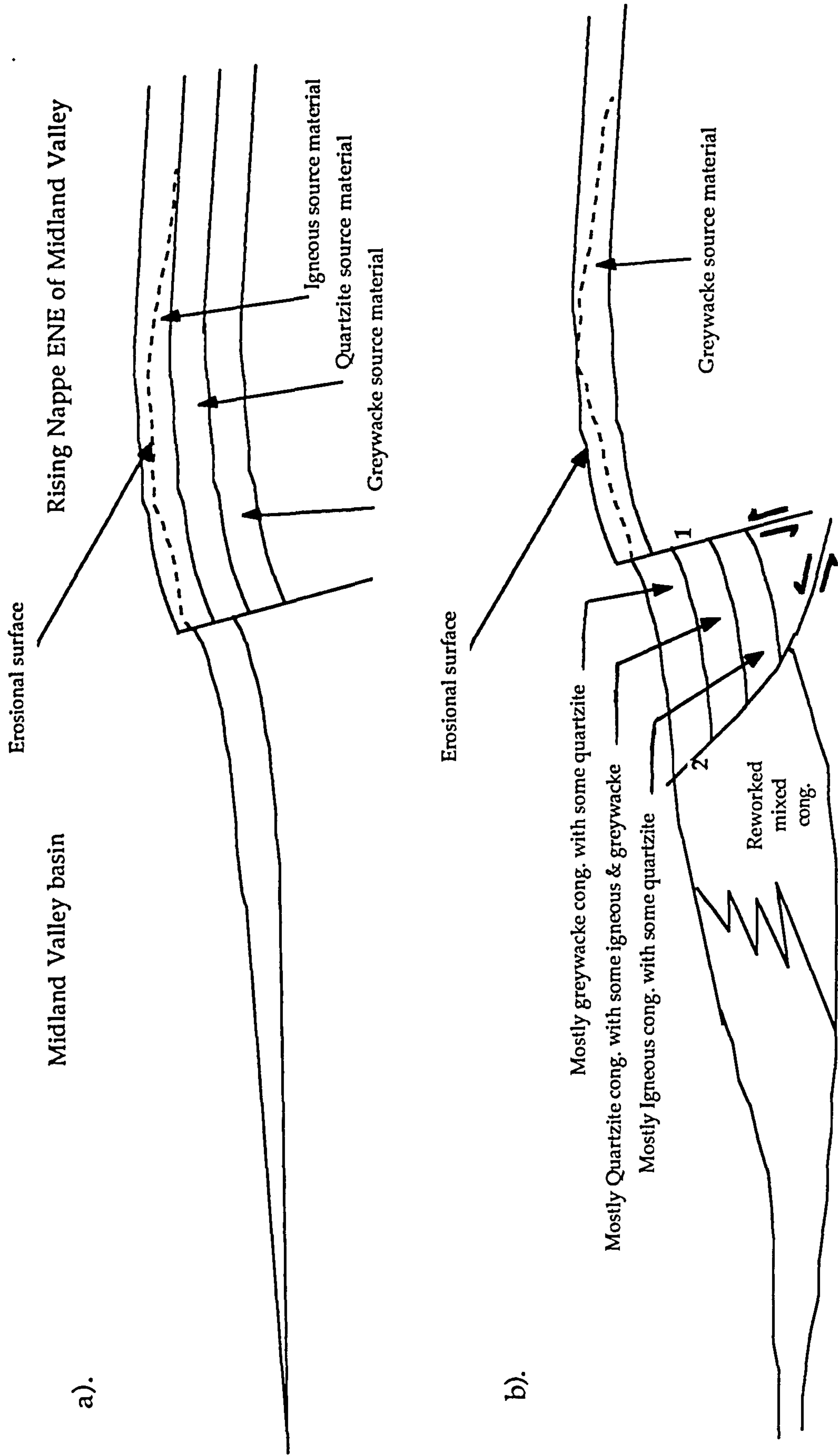


Fig. 6.4.2 Model 2: Deposition from a rising foreland thrust

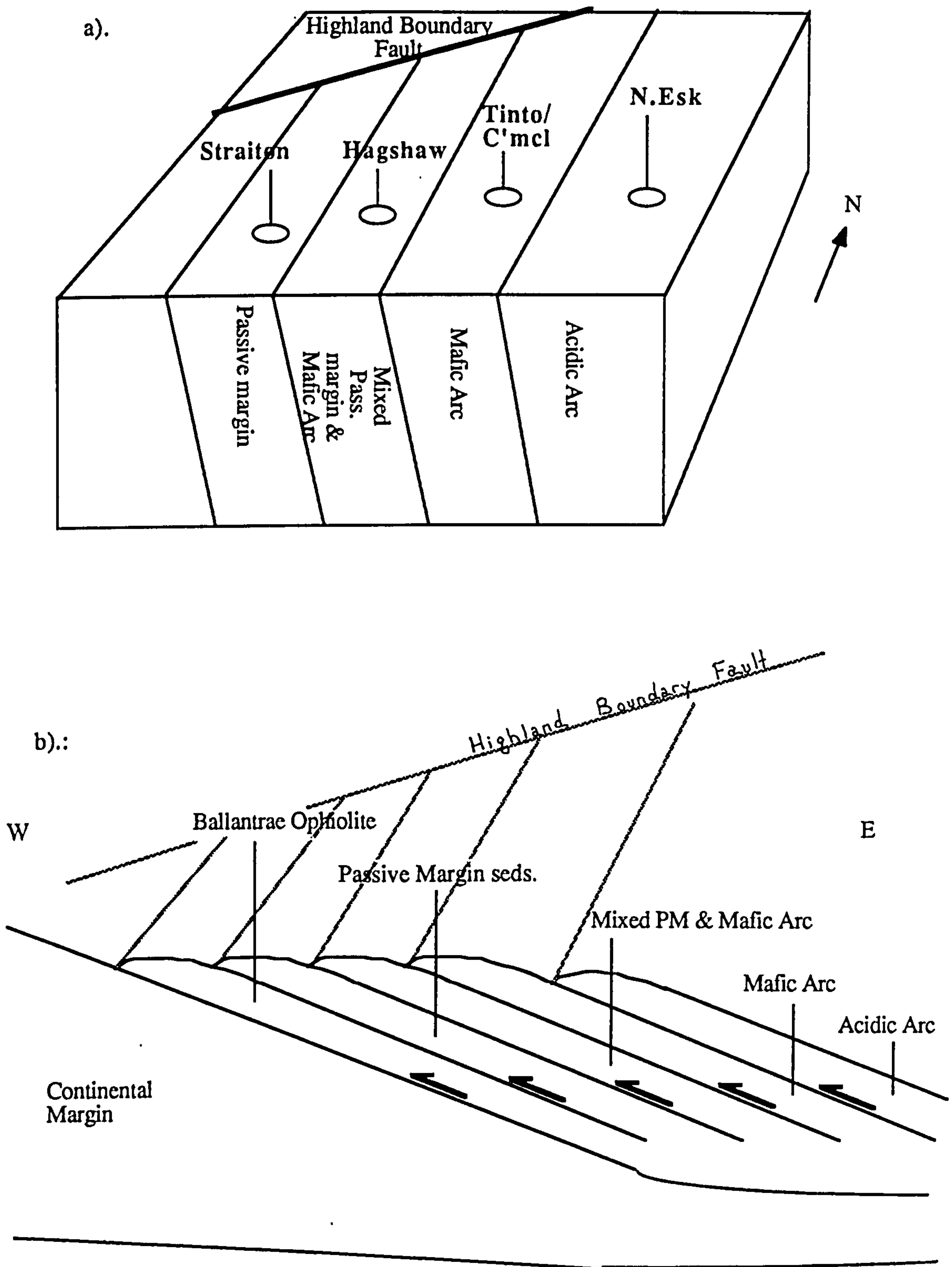
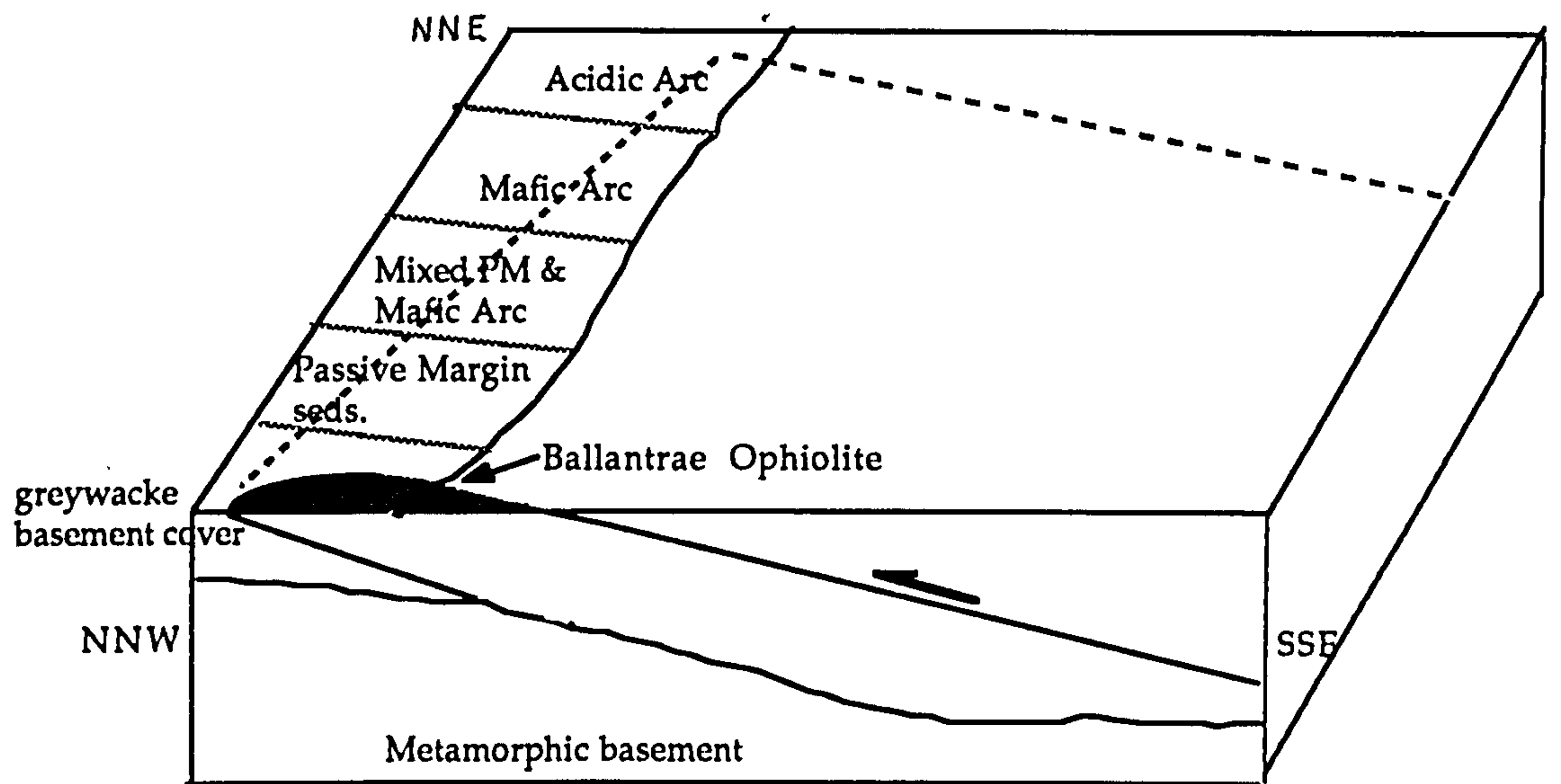


Fig. 6.4.3 a). Oblique petrographic trend in Midland Valley greywacke basement compared to Caledonian trend (the Highland Boundary Fault)

b). Hypothetical westward obduction of fore-arc sed. (see Fig. 6.1.1 b) and oceanic floor (Ballantrae Ophiolite) to account for oblique petrographic trend in greywacke basement



6.4.3 c). Accretion of Midland Valley greywacke basement cover prior to obduction of Ballantrae Ophiolite Complex

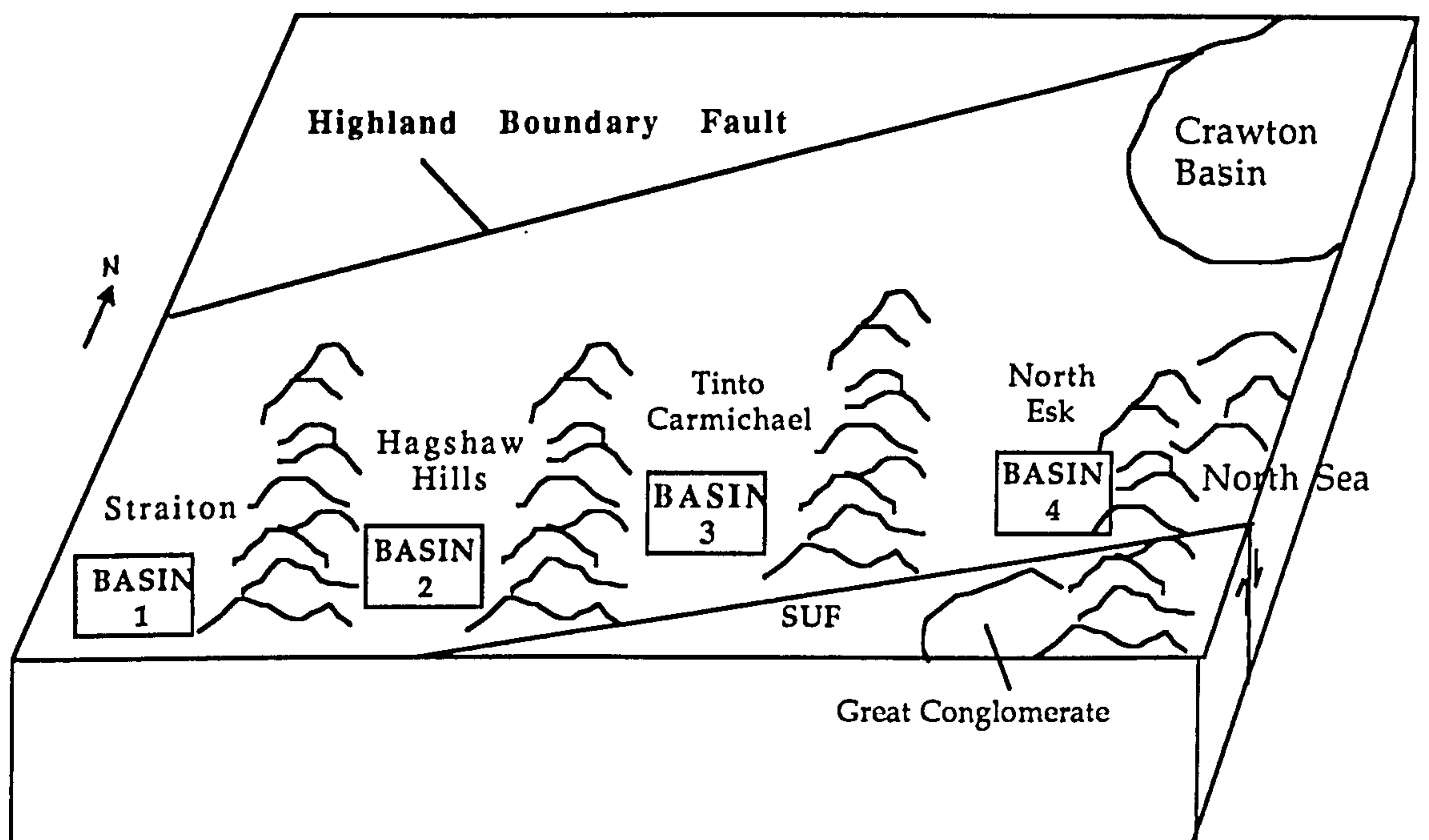


Fig. 6.4.4 a). Proposed sites of Greywacke basement highs

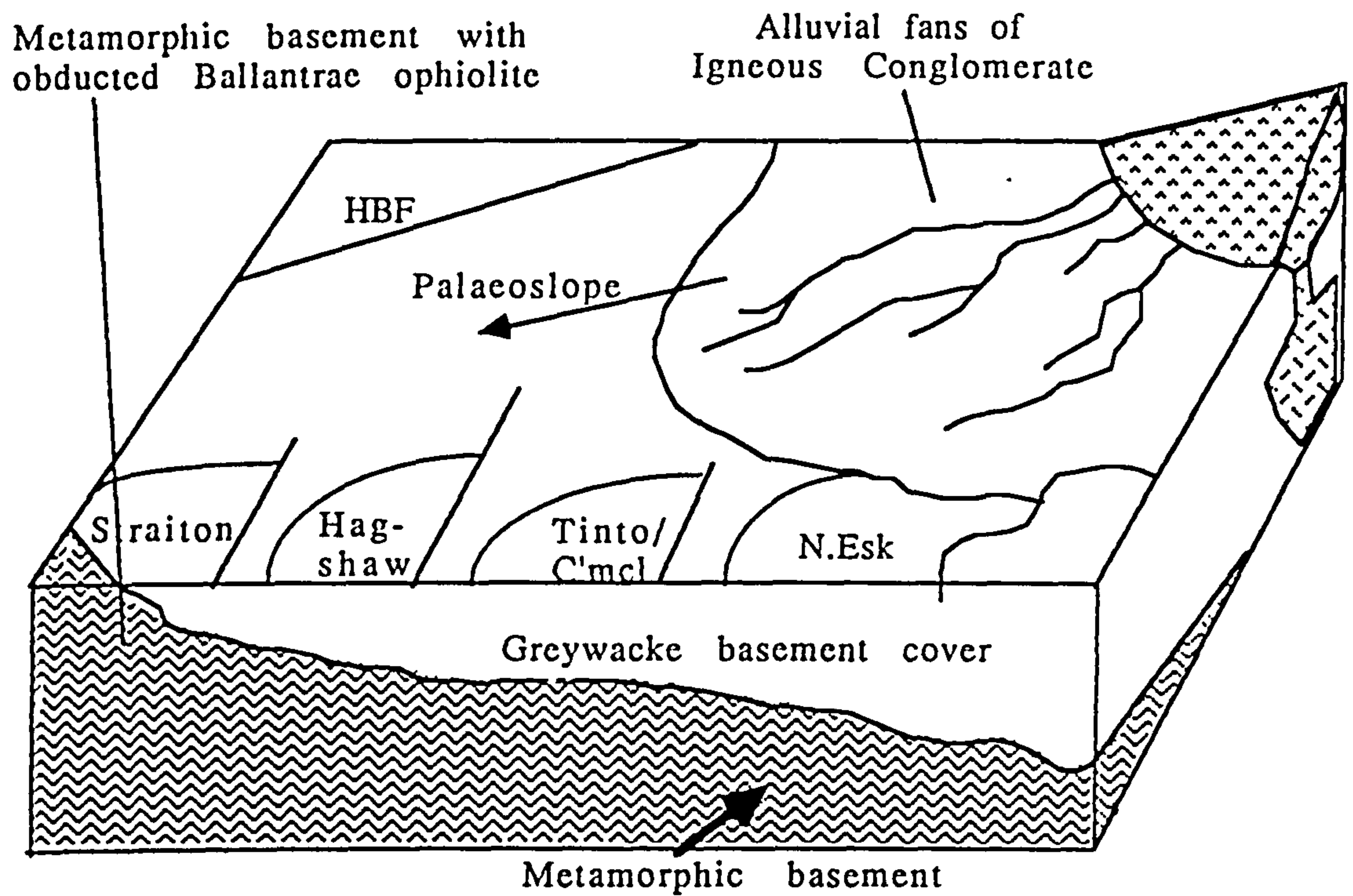


Fig. 6.4.4 c). Proposed site of uplift during Wenlock and origin of the Igneous Conglomerate

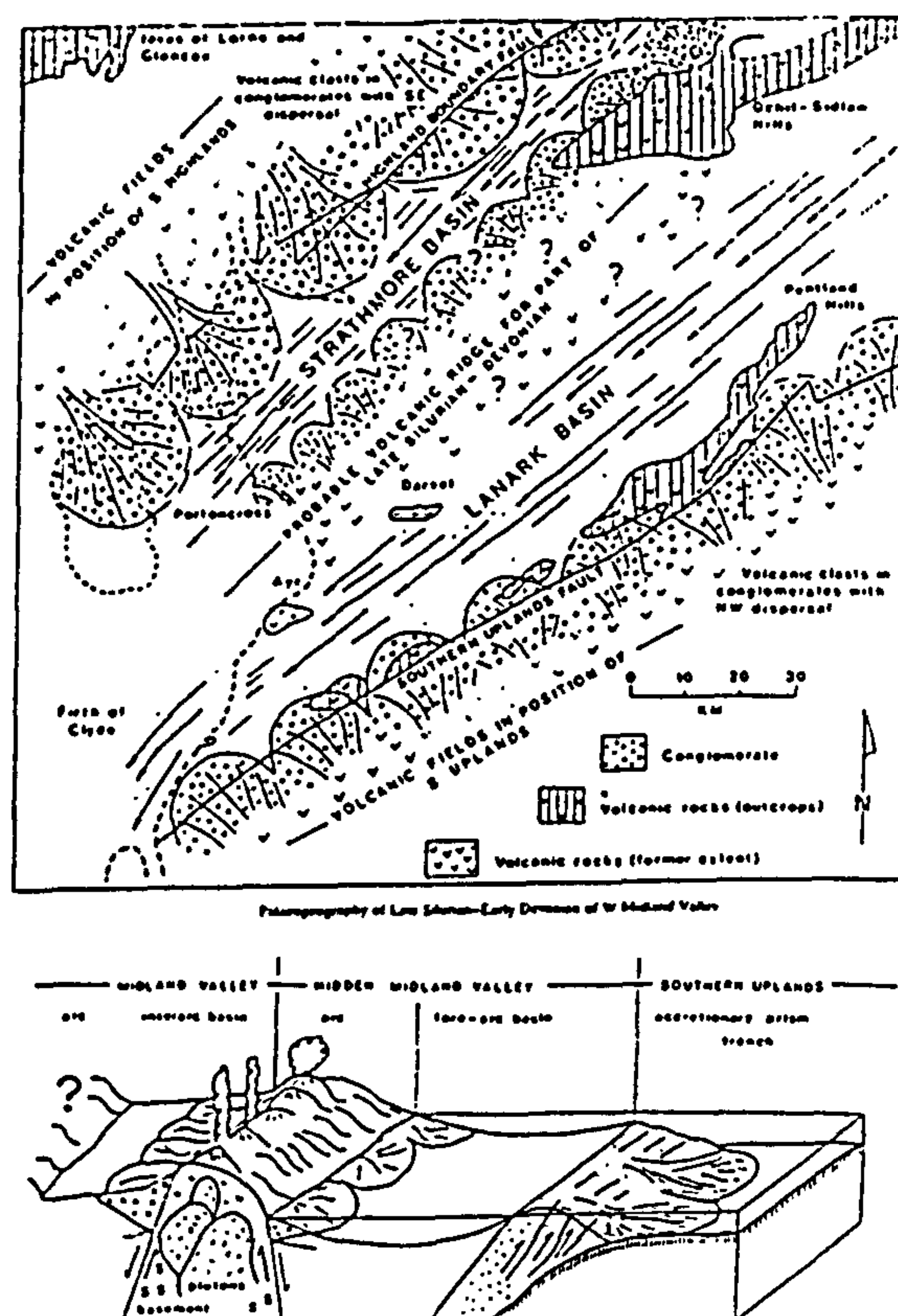


Fig. 6.2.1 Midland Valley arc-inter-arc theory after Bluck(1983) where igneous clasts are dispersed from a southerly source

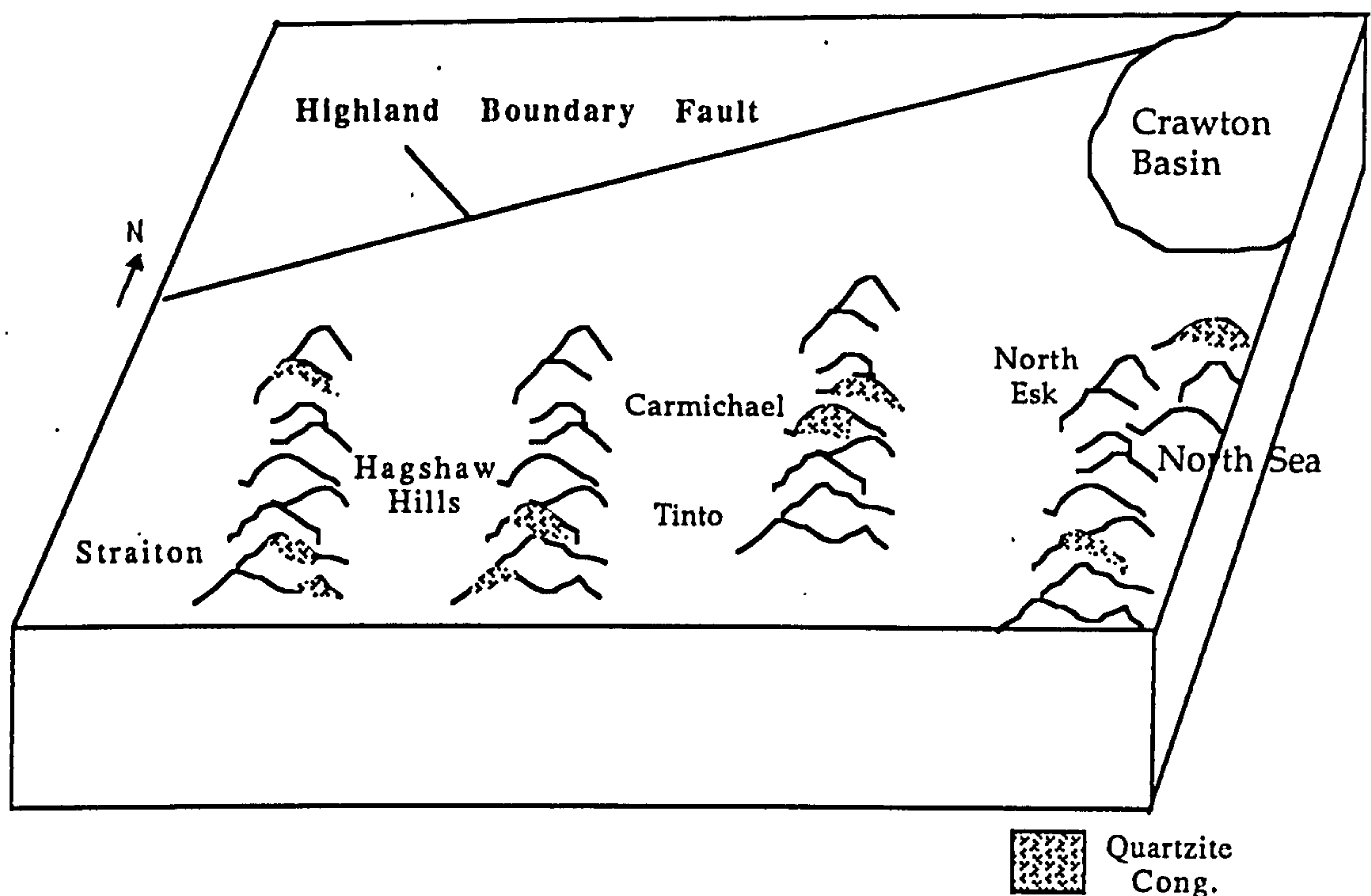


Fig. 6.4.4 c). Discontinuous cover of Quartzite Conglomerate on greywacke basement highs

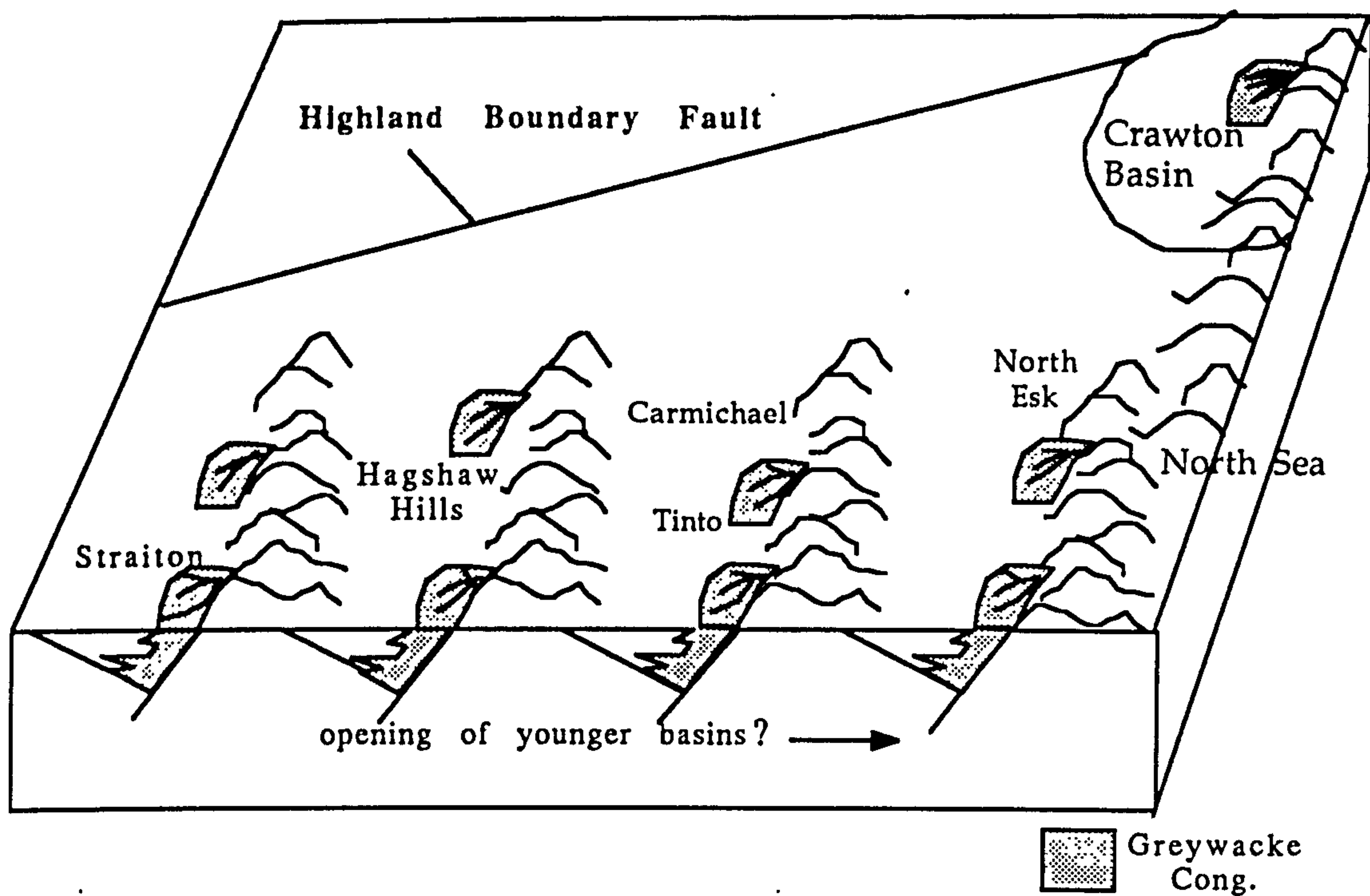
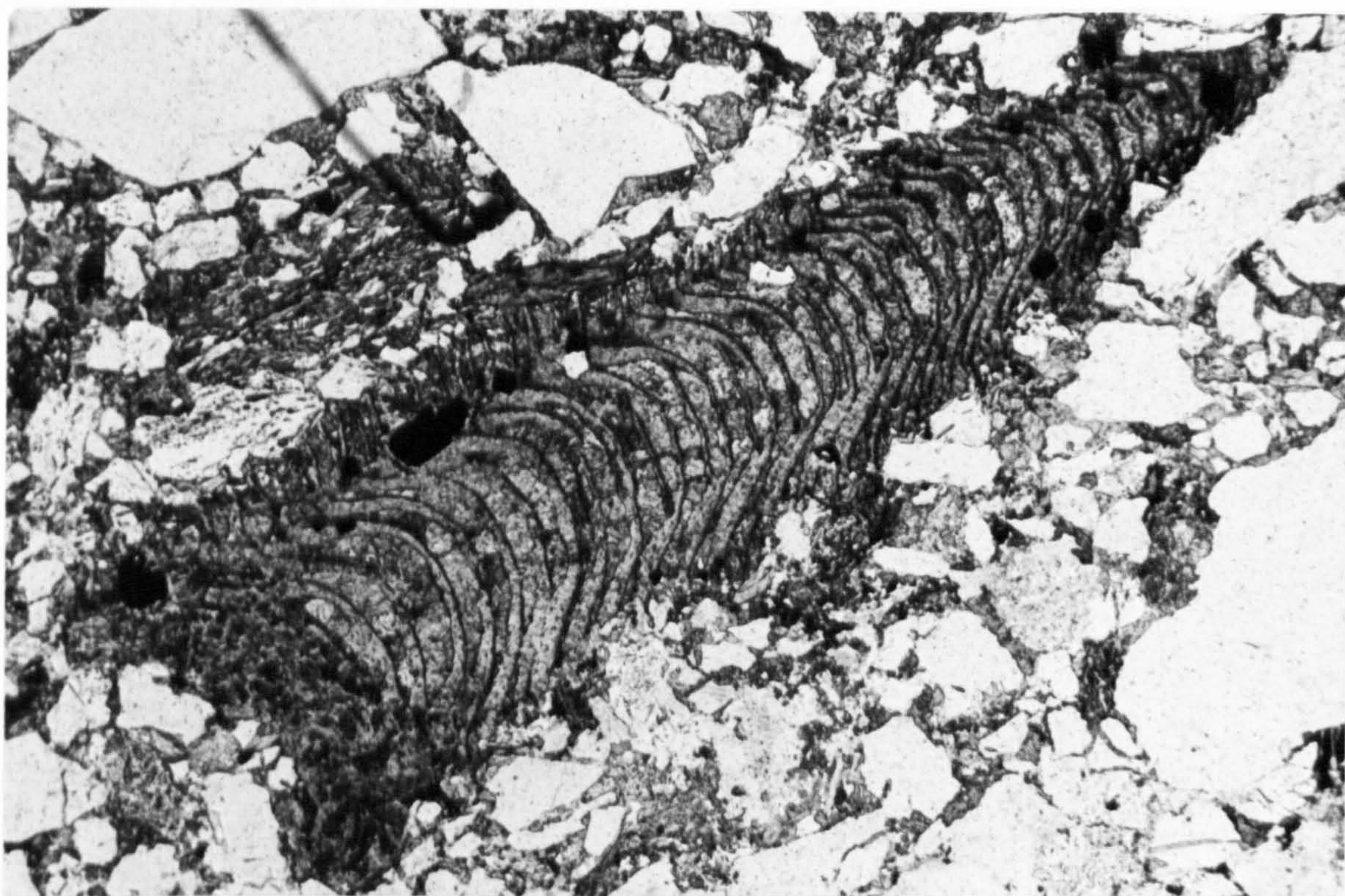


Fig. 6.4.4 d). Series of en echelon fault bounded Greywacke Conglomerate basins with dispersal from eastern marginal fault by small alluvial fans



6.1 Fossil in sandstone clast from Hagshaw Hills section 4.
x 50

7.0 Conclusions

The original purpose of the present study was to ascertain the relationship between the Southern Uplands block and the Midland Valley block during the uppermost Silurian-lowermost Devonian time interval. Specifically, did the Southern Uplands Fault control sedimentation during this time and was the Greywacke Conglomerate derived from the Southern Uplands Ordovician or Silurian sediments or both? It has been shown that the greywacke clasts in the Greywacke Conglomerate were not derived from either the Southern Uplands Silurian or Ordovician sediments and the Southern Uplands Fault or any ancestral equivalent did not control sedimentation during the uppermost Silurian. A number of important conclusions can also be drawn from the present study and are listed below.

- 1). The Silurian conglomerates all contain a fraction of acid-rich sedimentary clasts, the Greywacke Conglomerate is almost exclusively derived from this sedimentary source.
- 2). The dispersal of the southern Midland Valley Llandovery up to the Greywacke Conglomerate, uppermost Silurian, is equivocal but WSW-SSW dispersal for at least some of the succession and possibly including both the Igneous and Quartzite Conglomerates suggests the present day trace of the Southern Uplands Fault and the Southern Uplands did not control sedimentation during this time.
- 3). The deposition of the Greywacke Conglomerate can be dated at approximately the same age as the Tinto felsite, c. 410 Ma, and on the time scale of Harland *et al.* 1982 is Silurian.
- 4). The Greywacke Conglomerate was deposited as local fills in rapidly subsiding basins, each with one controlling border fault directly to the east.
- 5). The Great Conglomerate, which unconformably overlies the Southern Uplands Silurian succession, is similar to the Greywacke Conglomerate and shares the same easterly palaeoflow and indicates the Southern Uplands was a basin during this time.
- 6). The Lower Old Red Sandstone lithic arenite sandstone clasts in the northeastern Midland Valley are geochemically indistinguishable from the southern Midland Valley greywacke clasts, with the exception of the extremely high silica-rich sandstone clasts from the Straiton conglomerates. These sandstones all probably share the same source.

7). All of the clasts within the Greywacke Conglomerates are exceptionally quartz-rich, the drainage basin for the original turbidite assemblage was dominated by a quartz-rich metamorphic province.

8). The geochemical results revealed four distinct suites of sediments; i). the Southern Uplands Ordovician, ii). the Southern Uplands Silurian, iii). the southern Midland Valley greywacke clasts from the Hagshaw Hills northeastwards and including the Crawton Group sandstones and iv). the quartz-rich Straiton clasts.

9). Erosion of the source for the Greywacke Conglomerate records denudation of a coherent suite of sandstones from passive-margin through, mixed passive-margin immature arc, immature arc, and mature arc type-sandstones from the SW to the NE along the length of the Midland Valley, *i.e.* oblique to the same general petrographic trend in the Southern Uplands.

10). The model which best explains the origin for the Greywacke Conglomerate is uplift of pre-existing Midland Valley greywacke basement. This basement was accreted to the Midland Valley before deposition of the Igneous Conglomerate (pre-Wenlock) and possibly as early as pre-Arenig.

11). The Greywacke Conglomerate cannot be used as evidence for the timing of the emplacement of the Southern Uplands block as a whole or any particular unit within the block against the Midland Valley block.

12). There is no evidence for strike-slip fault control on a Caledonian NE-SW trending fault in the southern Midland Valley Old Red Sandstone basins. An alternative view is that much of the Upper Silurian-(?)Early Devonian Midland Valley may be related to extensional cratonic relaxation.

13). Accordingly, the Lower Old Red Sandstone lavas may not be related to northward subduction beneath the Midland Valley. Evidence from the Lava Conglomerate for volcanic fields south of the Southern Uplands Fault is inconclusive.

14). Assuming that the relative positions of the Scottish Caledonian structural blocks remain constant through geological time, a schematic evolutionary diagram of these structural blocks during the Lower Palaeozoic is shown in Fig. 7.1.

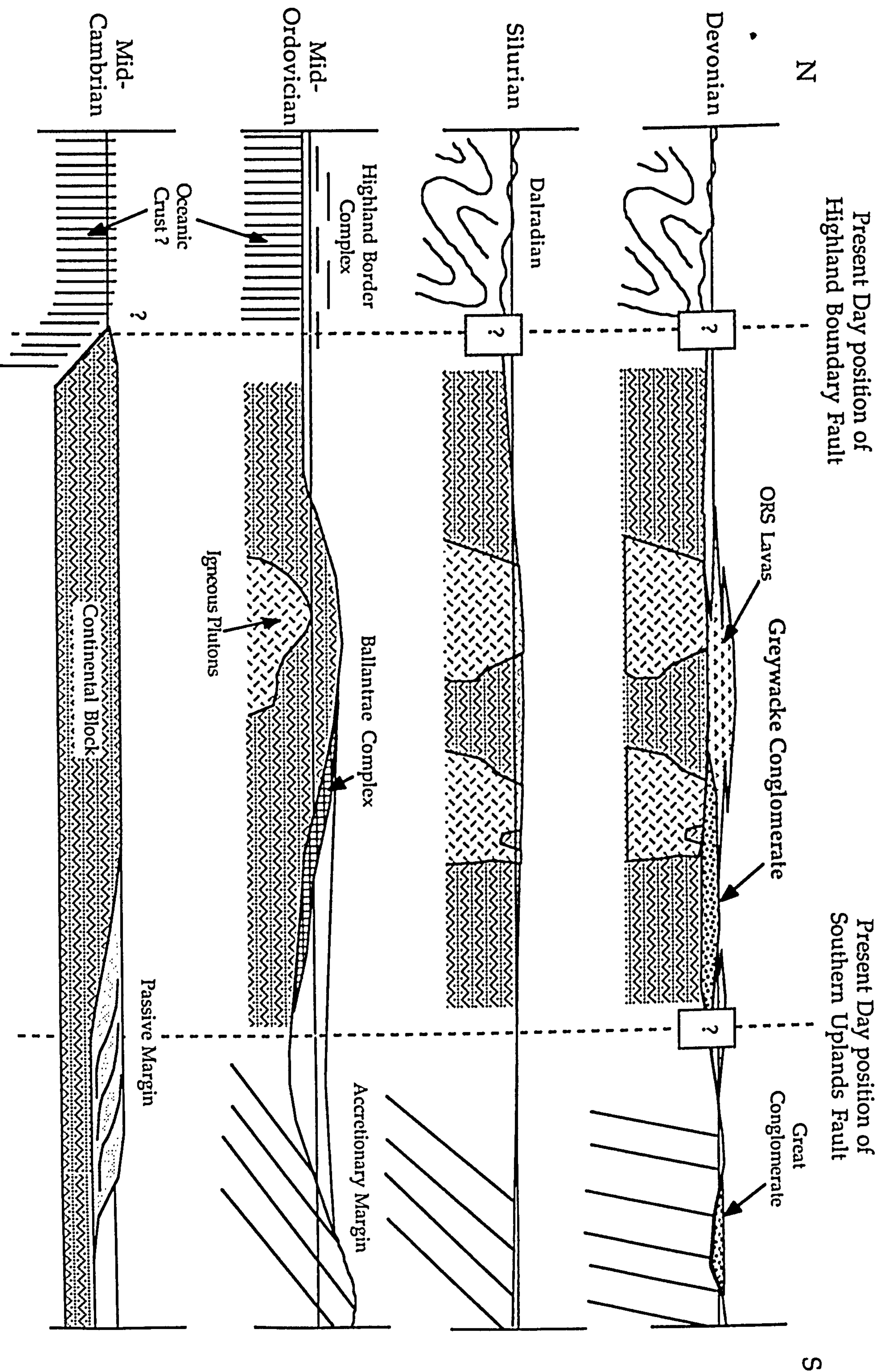


Figure 7.1 Evolution of the Midland Valley through the Lower Palaeozoic

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| Straiton | | | | | | | | | | | |
|----------|-----|-----|-------|------|------|------|-----|-----|-----|-----|-------|
| sample | qtz | fld | basic | acid | meta | sed. | alt | m-p | cmt | acc | total |
| 1-S-1 | 210 | 15 | 0 | 4 | 58 | 0 | 22 | 79 | 6 | 6 | 400 |
| 2-S-1 | 224 | 13 | 0 | 18 | 20 | 0 | 12 | 82 | 19 | 11 | 399 |
| 3-S-1 | 163 | 16 | 0 | 1 | 49 | 0 | 22 | 58 | 77 | 14 | 400 |
| 4-S-1 | 162 | 5 | 0 | 5 | 109 | 0 | 16 | 61 | 39 | 3 | 400 |
| 5-S-1 | 89 | 12 | 0 | 17 | 50 | 9 | 13 | 61 | 148 | 1 | 400 |
| 6-S-1 | 195 | 17 | 0 | 9 | 101 | 0 | 8 | 26 | 38 | 6 | 400 |
| 7-S-1 | 167 | 26 | 0 | 6 | 63 | 0 | 18 | 64 | 43 | 13 | 400 |
| 8-S-1 | 211 | 23 | 0 | 8 | 81 | 0 | 18 | 21 | 32 | 5 | 399 |
| 9-S-1 | 222 | 16 | 0 | 0 | 31 | 0 | 17 | 39 | 65 | 10 | 400 |
| 10-S-1 | 178 | 51 | 0 | 3 | 84 | 0 | 14 | 38 | 24 | 8 | 400 |
| 11-S-1 | 183 | 47 | 0 | 1 | 75 | 0 | 4 | 46 | 31 | 13 | 400 |
| 13-S-1 | 158 | 55 | 1 | 1 | 102 | 0 | 6 | 41 | 27 | 10 | 401 |
| 14-S-1 | 200 | 67 | 0 | 1 | 47 | 0 | 4 | 41 | 31 | 8 | 399 |
| 15-S-1 | 192 | 65 | 0 | 2 | 68 | 1 | 12 | 31 | 19 | 6 | 396 |
| 16-S-1 | 231 | 16 | 0 | 2 | 78 | 0 | 25 | 31 | 13 | 3 | 399 |
| 17-S-1 | 180 | 10 | 0 | 3 | 93 | 0 | 26 | 54 | 22 | 12 | 400 |
| 18-S-1 | 178 | 16 | 0 | 8 | 103 | 0 | 32 | 42 | 16 | 7 | 402 |
| 20-S-1 | 186 | 33 | 0 | 3 | 71 | 0 | 13 | 66 | 15 | 13 | 400 |
| 21-S-1 | 180 | 23 | 0 | 2 | 75 | 0 | 28 | 46 | 40 | 6 | 400 |
| 22-S-1 | 196 | 22 | 0 | 0 | 73 | 0 | 29 | 48 | 30 | 2 | 400 |

Straiton (cont.)

| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
|--------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| 23-S-1 | 198 | 6 | 0 | 7 | 73 | 0 | 30 | 46 | 31 | 9 | 400 |
| 24-S-1 | 202 | 14 | 0 | 3 | 76 | 0 | 22 | 54 | 23 | 6 | 400 |
| 25-S-1 | 213 | 11 | 0 | 4 | 69 | 0 | 34 | 34 | 26 | 9 | 400 |
| 26-S-1 | 182 | 43 | 2 | 10 | 100 | 0 | 23 | 32 | 6 | 4 | 402 |
| 27-S-1 | 207 | 42 | 0 | 2 | 62 | 0 | 24 | 38 | 15 | 10 | 400 |
| 31-S-1 | 174 | 47 | 0 | 0 | 66 | 0 | 16 | 37 | 52 | 8 | 400 |
| 1-S-2 | 212 | 24 | 0 | 2 | 51 | 1 | 12 | 39 | 32 | 27 | 400 |
| 2-S-2 | 138 | 19 | 0 | 11 | 58 | 1 | 32 | 17 | 116 | 8 | 400 |
| 4-S-2 | 132 | 56 | 1 | 4 | 64 | 0 | 34 | 3 | 89 | 20 | 403 |
| 5-S-2 | 183 | 69 | 0 | 3 | 66 | 0 | 10 | 41 | 5 | 20 | 397 |
| 7-S-2 | 176 | 54 | 2 | 8 | 58 | 0 | 12 | 66 | 11 | 13 | 400 |
| 8-S-2 | 126 | 41 | 0 | 9 | 89 | 0 | 20 | 35 | 63 | 17 | 400 |
| 10-S-2 | 154 | 57 | 0 | 4 | 59 | 1 | 30 | 57 | 30 | 18 | 410 |
| 11-S-2 | 184 | 55 | 0 | 5 | 69 | 0 | 9 | 42 | 21 | 12 | 397 |
| 12-S-2 | 142 | 58 | 4 | 9 | 115 | 0 | 16 | 38 | 11 | 7 | 400 |
| 13-S-2 | 165 | 43 | 0 | 3 | 88 | 0 | 21 | 45 | 23 | 13 | 401 |
| 14-S-2 | 148 | 60 | 0 | 7 | 36 | 0 | 15 | 75 | 56 | 3 | 400 |
| 15-S-2 | 219 | 75 | 0 | 0 | 19 | 0 | 6 | 31 | 30 | 20 | 400 |
| 16-S-2 | 154 | 56 | 0 | 9 | 90 | 0 | 13 | 30 | 36 | 12 | 400 |
| 18-S-2 | 222 | 50 | 1 | 9 | 75 | 0 | 4 | 33 | 6 | 0 | 400 |

| Straiton (cont.) | | | | | | | | | | | |
|------------------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
| 19-S-2 | 236 | 58 | 0 | 9 | 38 | 0 | 6 | 45 | 5 | 8 | 405 |
| 20-S-2 | 200 | 50 | 0 | 13 | 96 | 0 | 4 | 23 | 7 | 7 | 400 |
| 21-S-2 | 134 | 78 | 1 | 5 | 59 | 0 | 11 | 88 | 17 | 8 | 401 |
| 22-S-2 | 189 | 53 | 0 | 7 | 73 | 0 | 5 | 51 | 10 | 12 | 400 |
| 23-S-2 | 153 | 48 | 9 | 13 | 98 | 0 | 25 | 24 | 13 | 7 | 390 |
| 24-S-2 | 150 | 36 | 9 | 21 | 102 | 1 | 18 | 32 | 25 | 6 | 400 |
| 25-S-2 | 153 | 31 | 0 | 5 | 77 | 2 | 28 | 63 | 26 | 15 | 400 |
| 26-S-2 | 201 | 55 | 0 | 1 | 55 | 1 | 9 | 52 | 9 | 16 | 399 |
| 28-S-2 | 179 | 74 | 0 | 2 | 77 | 0 | 17 | 38 | 10 | 3 | 400 |
| 29-S-2 | 155 | 64 | 5 | 18 | 96 | 0 | 16 | 32 | 5 | 12 | 403 |
| 30-S-2 | 125 | 45 | 1 | 3 | 68 | 2 | 37 | 23 | 78 | 18 | 400 |
| 31-S-2 | 120 | 61 | 17 | 8 | 77 | 0 | 30 | 76 | 0 | 10 | 399 |
| 32-S-2 | 189 | 50 | 2 | 6 | 93 | 0 | 10 | 31 | 11 | 8 | 400 |
| 33-S-2 | 160 | 40 | 0 | 2 | 112 | 1 | 10 | 36 | 6 | 3 | 370 |
| 34-S-2 | 158 | 55 | 0 | 9 | 111 | 0 | 6 | 53 | 3 | 6 | 401 |
| 35-S-2 | 125 | 51 | 8 | 10 | 98 | 0 | 22 | 63 | 3 | 10 | 390 |
| 36-S-2 | 165 | 65 | 1 | 4 | 90 | 0 | 7 | 32 | 43 | 13 | 420 |
| 38-S-2 | 181 | 59 | 1 | 10 | 86 | 0 | 11 | 27 | 5 | 18 | 398 |
| 39-S-2 | 162 | 55 | 0 | 0 | 68 | 0 | 5 | 80 | 17 | 11 | 398 |

Hagslaw Hills

| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
|--------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| 1-H-1 | 156 | 43 | 1 | 17 | 37 | 0 | 24 | 84 | 33 | 6 | 401 |
| 2-H-1 | 124 | 51 | 9 | 19 | 10 | 0 | 18 | 2 | 157 | 9 | 399 |
| 3-H-1 | 145 | 54 | 5 | 15 | 22 | 0 | 5 | 49 | 95 | 8 | 398 |
| 4-H-1 | 169 | 64 | 4 | 25 | 53 | 1 | 14 | 34 | 33 | 6 | 403 |
| 5-H-1 | 184 | 60 | 3 | 18 | 32 | 0 | 26 | 50 | 12 | 14 | 399 |
| 6-H-1 | 218 | 46 | 1 | 3 | 48 | 0 | 7 | 37 | 10 | 30 | 400 |
| 7-H-1 | 157 | 50 | 21 | 53 | 49 | 4 | 24 | 12 | 24 | 5 | 399 |
| 9-H-1 | 140 | 34 | 1 | 2 | 26 | 0 | 20 | 0 | 161 | 16 | 400 |
| 10-H-1 | 181 | 57 | 5 | 17 | 77 | 1 | 16 | 21 | 11 | 13 | 399 |
| 11-H-1 | 155 | 72 | 9 | 50 | 69 | 0 | 15 | 10 | 16 | 4 | 400 |
| 12-H-1 | 161 | 73 | 9 | 19 | 44 | 0 | 24 | 26 | 34 | 13 | 403 |
| 14-H-1 | 220 | 32 | 0 | 18 | 31 | 0 | 30 | 38 | 17 | 14 | 400 |
| 15-H-1 | 176 | 54 | 3 | 8 | 69 | 0 | 20 | 49 | 7 | 14 | 400 |
| 16-H-1 | 151 | 71 | 5 | 14 | 72 | 0 | 21 | 40 | 15 | 11 | 400 |
| 17-H-1 | 122 | 92 | 13 | 31 | 46 | 6 | 26 | 46 | 10 | 7 | 399 |
| 18-H-1 | 202 | 42 | 2 | 11 | 66 | 0 | 12 | 18 | 32 | 14 | 399 |
| 19-H-1 | 108 | 46 | 4 | 6 | 58 | 1 | 23 | 0 | 145 | 9 | 400 |
| 20-H-1 | 143 | 44 | 8 | 11 | 58 | 0 | 32 | 0 | 96 | 8 | 400 |
| 21-H-1 | 130 | 72 | 11 | 20 | 17 | 3 | 47 | 5 | 88 | 7 | 400 |
| 1-H-3 | 146 | 60 | 6 | 22 | 52 | 0 | 19 | 48 | 31 | 16 | 400 |

Flagshaw Hills (cont.)

| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
|--------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| 2-H-3 | 138 | 75 | 10 | 37 | 27 | 1 | 14 | 50 | 27 | 21 | 400 |
| 3-H-3 | 190 | 71 | 0 | 4 | 25 | 0 | 2 | 65 | 7 | 22 | 386 |
| 4-H-3 | 150 | 78 | 2 | 22 | 18 | 0 | 21 | 65 | 29 | 15 | 400 |
| 5-H-3 | 184 | 70 | 5 | 21 | 29 | 0 | 16 | 56 | 12 | 6 | 399 |
| 6-H-3 | 119 | 33 | 0 | 21 | 6 | 1 | 19 | 78 | 112 | 9 | 398 |
| 11-H-3 | 124 | 34 | 4 | 15 | 25 | 0 | 27 | 44 | 112 | 9 | 394 |
| 12-H-3 | 161 | 35 | 12 | 46 | 41 | 6 | 16 | 22 | 61 | 3 | 403 |
| 13-H-3 | 185 | 66 | 4 | 28 | 38 | 0 | 18 | 43 | 9 | 8 | 399 |
| 14-H-3 | 153 | 72 | 1 | 17 | 54 | 0 | 27 | 46 | 16 | 13 | 399 |
| 15-H-3 | 141 | 61 | 11 | 32 | 46 | 1 | 19 | 22 | 54 | 14 | 401 |
| 17-H-3 | 211 | 65 | 0 | 5 | 23 | 2 | 24 | 41 | 20 | 10 | 401 |
| 18-H-3 | 126 | 62 | 3 | 27 | 77 | 7 | 16 | 44 | 31 | 7 | 400 |
| 19-H-3 | 160 | 58 | 0 | 22 | 87 | 0 | 7 | 40 | 16 | 10 | 400 |
| 1-H-4 | 151 | 41 | 1 | 12 | 57 | 0 | 14 | 7 | 109 | 8 | 400 |
| 2-H-4 | 176 | 41 | 1 | 11 | 90 | 0 | 11 | 38 | 16 | 16 | 400 |
| 3-H-4 | 219 | 26 | 3 | 12 | 18 | 0 | 17 | 51 | 37 | 17 | 400 |

| sample | qtz | fld | basic | acid | Tinto-Carmichael | | alt | m-p | cmt | acc | total |
|--------|-----|-----|-------|------|------------------|-----|-----|-----|-----|-----|-------|
| | | | | | meta | sed | | | | | |
| 3-T-1 | 101 | 111 | 8 | 14 | 50 | 1 | 21 | 85 | 1 | 7 | 399 |
| 4-T-1 | 175 | 79 | 12 | 25 | 35 | 0 | 5 | 59 | 3 | 7 | 400 |
| 5-T-1 | 87 | 67 | 65 | 41 | 25 | 2 | 44 | 48 | 7 | 14 | 400 |
| 6-T-1 | 161 | 44 | 11 | 16 | 73 | 0 | 15 | 58 | 7 | 15 | 400 |
| 7-T-1 | 132 | 69 | 7 | 14 | 74 | 0 | 12 | 72 | 2 | 18 | 400 |
| 8-T-1 | 131 | 55 | 3 | 8 | 68 | 0 | 24 | 76 | 25 | 10 | 400 |
| 9-T-1 | 169 | 68 | 10 | 13 | 57 | 0 | 18 | 49 | 3 | 13 | 400 |
| 10-T-1 | 190 | 57 | 19 | 19 | 50 | 1 | 13 | 39 | 8 | 3 | 399 |
| 11-T-1 | 152 | 91 | 3 | 9 | 23 | 0 | 15 | 80 | 5 | 22 | 400 |
| 12-T-1 | 121 | 71 | 6 | 14 | 64 | 0 | 17 | 96 | 1 | 10 | 400 |
| 13-T-1 | 181 | 62 | 13 | 13 | 50 | 1 | 14 | 57 | 2 | 6 | 399 |
| 14-T-1 | 132 | 68 | 6 | 14 | 46 | 0 | 14 | 102 | 6 | 13 | 401 |
| 16-T-1 | 175 | 67 | 16 | 11 | 29 | 0 | 22 | 52 | 24 | 4 | 400 |
| 17-T-1 | 151 | 47 | 14 | 9 | 90 | 2 | 14 | 57 | 6 | 10 | 400 |
| 1-C-1 | 172 | 56 | 13 | 8 | 71 | 0 | 18 | 34 | 8 | 19 | 399 |
| 2-C-1 | 170 | 81 | 2 | 12 | 30 | 0 | 15 | 73 | 13 | 4 | 400 |
| 3-C-1 | 175 | 73 | 0 | 0 | 28 | 0 | 8 | 75 | 14 | 27 | 400 |
| 4-C-1 | 159 | 72 | 1 | 5 | 71 | 0 | 6 | 64 | 3 | 18 | 399 |
| 5-C-1 | 65 | 130 | 32 | 56 | 0 | 0 | 43 | 47 | 9 | 8 | 390 |
| 6-C-1 | 189 | 49 | 3 | 26 | 45 | 0 | 8 | 68 | 9 | 3 | 400 |
| 7-C-1 | 209 | 58 | 10 | 6 | 54 | 1 | 19 | 26 | 5 | 13 | 401 |

North Esk

| sample | qlz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
|---------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| 1-NE-1 | 175 | 73 | 11 | 10 | 50 | 0 | 15 | 40 | 6 | 21 | 401 |
| 2-NE-1 | 148 | 91 | 9 | 11 | 58 | 0 | 20 | 45 | 5 | 13 | 400 |
| 3-NE-1 | 141 | 67 | 8 | 9 | 33 | 0 | 17 | 86 | 5 | 20 | 386 |
| 4-NE-1 | 177 | 88 | 11 | 14 | 30 | 0 | 15 | 46 | 5 | 13 | 399 |
| 5-NE-1 | 154 | 81 | 11 | 15 | 49 | 0 | 18 | 53 | 11 | 8 | 400 |
| 7-NE-1 | 173 | 73 | 6 | 25 | 26 | 0 | 14 | 58 | 19 | 6 | 400 |
| 8-NE-1 | 136 | 77 | 14 | 8 | 60 | 0 | 21 | 76 | 4 | 4 | 400 |
| 9-NE-1 | 155 | 90 | 5 | 1 | 28 | 0 | 22 | 63 | 30 | 6 | 400 |
| 10-NE-1 | 140 | 95 | 18 | 16 | 68 | 0 | 15 | 34 | 2 | 12 | 400 |
| 11-NE-1 | 172 | 80 | 7 | 16 | 32 | 0 | 15 | 55 | 10 | 12 | 399 |
| 12-NE-1 | 123 | 106 | 6 | 12 | 52 | 0 | 14 | 70 | 10 | 7 | 400 |
| 13-NE-1 | 132 | 91 | 9 | 12 | 47 | 0 | 18 | 68 | 15 | 8 | 400 |
| 14-NE-1 | 167 | 73 | 6 | 6 | 50 | 0 | 6 | 82 | 5 | 1 | 396 |
| 15-NE-1 | 160 | 61 | 10 | 19 | 77 | 0 | 14 | 47 | 10 | 2 | 400 |
| 16-NE-1 | 144 | 93 | 11 | 14 | 53 | 0 | 11 | 59 | 11 | 4 | 400 |
| 17-NE-1 | 154 | 83 | 5 | 13 | 48 | 0 | 15 | 62 | 12 | 7 | 399 |
| 18-NE-1 | 142 | 76 | 10 | 9 | 57 | 0 | 25 | 54 | 22 | 5 | 400 |
| 19-NE-1 | 184 | 61 | 14 | 18 | 54 | 0 | 25 | 28 | 8 | 8 | 400 |
| 20-NE-1 | 128 | 79 | 11 | 9 | 42 | 0 | 15 | 22 | 31 | 3 | 340 |
| 21-NE-1 | 190 | 64 | 7 | 27 | 37 | 0 | 18 | 50 | 6 | 1 | 400 |

North Esk (cont.)

| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
|---------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| 22-NE-1 | 136 | 90 | 4 | 5 | 53 | 0 | 15 | 68 | 21 | 8 | 400 |
| 23-NE-1 | 146 | 83 | 16 | 4 | 40 | 1 | 22 | 52 | 21 | 16 | 401 |
| 24-NE-1 | 142 | 87 | 20 | 16 | 42 | 0 | 22 | 39 | 28 | 5 | 401 |
| 25-NE-1 | 137 | 91 | 9 | 13 | 45 | 1 | 24 | 51 | 21 | 10 | 402 |
| 1-NE-2 | 117 | 68 | 17 | 16 | 31 | 0 | 23 | 44 | 80 | 4 | 400 |
| 2-NE-2 | 129 | 87 | 12 | 12 | 35 | 0 | 16 | 83 | 16 | 10 | 400 |
| 3-NE-2 | 189 | 63 | 5 | 16 | 47 | 0 | 18 | 49 | 13 | 0 | 400 |
| 4-NE-2 | 165 | 66 | 13 | 15 | 56 | 2 | 9 | 50 | 20 | 5 | 401 |
| 5-NE-2 | 178 | 64 | 16 | 21 | 42 | 1 | 18 | 47 | 9 | 4 | 400 |
| 6-NE-2 | 196 | 70 | 9 | 16 | 38 | 1 | 22 | 38 | 2 | 8 | 400 |
| 9-NE-2 | 152 | 78 | 11 | 12 | 53 | 0 | 14 | 61 | 9 | 10 | 400 |
| 10-NE-2 | 206 | 64 | 19 | 17 | 45 | 1 | 13 | 25 | 4 | 7 | 401 |
| 11-NE-2 | 156 | 84 | 4 | 7 | 59 | 0 | 17 | 50 | 19 | 5 | 401 |
| 12-NE-2 | 174 | 65 | 10 | 16 | 44 | 0 | 11 | 68 | 9 | 3 | 400 |
| 13-NE-2 | 149 | 65 | 46 | 32 | 24 | 0 | 19 | 57 | 8 | 1 | 401 |
| 15-NE-2 | 168 | 66 | 15 | 9 | 49 | 1 | 18 | 59 | 6 | 9 | 400 |
| 17-NE-2 | 165 | 79 | 18 | 6 | 38 | 0 | 14 | 60 | 9 | 10 | 399 |
| 18-NE-2 | 141 | 81 | 7 | 15 | 34 | 0 | 29 | 62 | 26 | 5 | 400 |
| 19-NE-2 | 141 | 72 | 6 | 30 | 48 | 0 | 23 | 74 | 5 | 1 | 400 |
| 21-NE-2 | 205 | 39 | 20 | 14 | 51 | 0 | 23 | 30 | 16 | 3 | 401 |

| North Esk (cont.) | | | | | | | | | | | |
|-------------------|-----|-----|-------|------|------|-----|-----|-----|-----|-----|-------|
| sample | qtz | fld | basic | acid | meta | sed | alt | m-p | cmt | acc | total |
| 22-NE-2 | 139 | 62 | 23 | 18 | 45 | 0 | 23 | 45 | 38 | 7 | 400 |
| 23-NE-2 | 157 | 88 | 1 | 10 | 50 | 0 | 25 | 51 | 15 | 3 | 400 |
| 24-NE-2 | 149 | 65 | 20 | 25 | 61 | 0 | 13 | 46 | 10 | 10 | 399 |
| 25-NE-2 | 110 | 89 | 15 | 11 | 55 | 1 | 14 | 84 | 5 | 16 | 400 |
| 26-NE-2 | 125 | 96 | 10 | 7 | 57 | 0 | 14 | 77 | 9 | 5 | 400 |
| 1-NE-3 | 128 | 125 | 4 | 45 | 2 | 0 | 26 | 53 | 9 | 8 | 400 |
| 2-NE-3 | 106 | 139 | 8 | 55 | 6 | 0 | 24 | 51 | 8 | 3 | 400 |
| 1-NE-4 | 78 | 53 | 6 | 2 | 60 | 1 | 36 | 24 | 132 | 13 | 405 |
| 2-NE-4 | 108 | 56 | 1 | 6 | 14 | 0 | 10 | 50 | 147 | 8 | 400 |
| 4-NE-4 | 172 | 52 | 8 | 15 | 69 | 0 | 27 | 49 | 3 | 6 | 401 |
| 5-NE-4 | 169 | 55 | 11 | 5 | 70 | 0 | 16 | 55 | 9 | 10 | 400 |
| 6-NE-4 | 167 | 74 | 5 | 7 | 47 | 0 | 24 | 58 | 7 | 10 | 399 |
| 7-NE-4 | 180 | 77 | 4 | 27 | 48 | 0 | 16 | 33 | 10 | 4 | 399 |
| 1-NE-5 | 201 | 51 | 2 | 5 | 14 | 0 | 37 | 54 | 32 | 4 | 400 |
| 2-NE-5 | 193 | 35 | 0 | 10 | 49 | 0 | 37 | 55 | 17 | 4 | 400 |
| 3-NE-5 | 170 | 44 | 1 | 6 | 36 | 0 | 43 | 72 | 11 | 16 | 399 |

| | <i>Granule</i> | | | | | | | | |
|---------|----------------|-----|-------|------|------|-----|-----|-------|-------|
| | qtz | fld | basic | acid | meta | sed | alt | other | total |
| 12-S-1 | 51 | 5 | 0 | 6 | 34 | 3 | 1 | 0 | 100 |
| 19-S-1 | 52 | 1 | 0 | 8 | 38 | 0 | 1 | 0 | 100 |
| 28-S-1 | 55 | 0 | 1 | 4 | 32 | 0 | 8 | 0 | 100 |
| 29-S-1 | 45 | 1 | 0 | 8 | 44 | 0 | 3 | 0 | 101 |
| 30-S-1 | 49 | 3 | 0 | 6 | 39 | 1 | 2 | 0 | 100 |
| 6-S-2 | 37 | 3 | 0 | 10 | 45 | 2 | 3 | 0 | 100 |
| 17-S-2 | 45 | 5 | 0 | 5 | 43 | 0 | 2 | 0 | 100 |
| 27-S-2 | 49 | 2 | 4 | 7 | 35 | 3 | 1 | 0 | 100 |
| 37-S-2 | 44 | 1 | 2 | 7 | 45 | 1 | 0 | 0 | 100 |
| 40-S-2 | 41 | 6 | 11 | 23 | 19 | 0 | 0 | 0 | 100 |
| 8-H-1 | 30 | 2 | 15 | 30 | 19 | 3 | 1 | 0 | 100 |
| 13-H-1 | 24 | 17 | 9 | 31 | 18 | 1 | 0 | 0 | 100 |
| 22-H-1 | 49 | 5 | 4 | 11 | 28 | 1 | 1 | 1 | 100 |
| 7-H-3 | 31 | 9 | 5 | 17 | 35 | 2 | 0 | 0 | 99 |
| 8-H-3 | 31 | 9 | 17 | 29 | 13 | 1 | 0 | 0 | 100 |
| 9-H-3 | 51 | 1 | 2 | 1 | 32 | 7 | 2 | 4 | 100 |
| 16-H-3 | 21 | 4 | 12 | 36 | 9 | 15 | 3 | 0 | 100 |
| 6-NE-1 | 49 | 5 | 19 | 15 | 12 | 0 | 0 | 0 | 100 |
| 8-NE-2 | 51 | 11 | 3 | 28 | 7 | 0 | 0 | 0 | 100 |
| 14-NE-2 | 28 | 3 | 17 | 33 | 14 | 5 | 0 | 0 | 100 |
| 16-NE-2 | 53 | 5 | 18 | 13 | 10 | 1 | 0 | 0 | 100 |
| 3-NE-3 | 46 | 6 | 5 | 12 | 24 | 0 | 0 | 0 | 93 |
| 8-NE-4 | 16 | 3 | 17 | 56 | 5 | 3 | 0 | 0 | 100 |

Straiton

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 1-S-1 | 15 | 7 | 2 | 0 | 2 | 0 | 0 | 0 |
| 2-S-1 | 37 | 14 | 0 | 0 | 9 | 0 | 0 | 0 |
| 3-S-1 | 11 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4-S-1 | 11 | 5 | 0 | 0 | 0 | 1 | 0 | 0 |
| 5-S-1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 |
| 6-S-1 | 12 | 6 | 0 | 0 | 5 | 0 | 0 | 0 |
| 7-S-1 | 17 | 10 | 0 | 0 | 4 | 0 | 1 | 0 |
| 8-S-1 | 11 | 7 | 0 | 0 | 2 | 0 | 2 | 0 |
| 9-S-1 | 35 | 20 | 0 | 0 | 4 | 0 | 5 | 0 |
| 10-S-1 | 5 | 0 | 0 | 0 | 3 | 0 | 1 | 0 |
| 11-S-1 | 13 | 8 | 0 | 0 | 8 | 0 | 1 | 0 |
| 13-S-1 | 8 | 4 | 0 | 2 | 3 | 0 | 1 | 0 |
| 14-S-1 | 10 | 5 | 0 | 0 | 5 | 0 | 2 | 0 |
| 15-S-1 | 8 | 5 | 0 | 1 | 3 | 0 | 1 | 0 |
| 16-S-1 | 1 | 1 | 0 | 0 | 0 | 0 | 2 | 0 |
| 17-S-1 | 18 | 6 | 0 | 0 | 5 | 0 | 1 | 0 |
| 18-S-1 | 6 | 3 | 0 | 0 | 4 | 0 | 1 | 0 |
| 20-S-1 | 6 | 12 | 0 | 0 | 2 | 0 | 0 | 0 |
| 21-S-1 | 9 | 7 | 0 | 0 | 3 | 0 | 0 | 0 |
| 22-S-1 | 6 | 2 | 0 | 0 | 4 | 0 | 0 | 0 |
| 23-S-1 | 8 | 6 | 0 | 0 | 2 | 0 | 2 | 0 |
| 24-S-1 | 18 | 10 | 0 | 0 | 9 | 0 | 3 | 0 |
| 25-S-1 | 7 | 8 | 0 | 0 | 9 | 0 | 0 | 0 |
| 26-S-1 | 3 | 2 | 0 | 0 | 5 | 0 | 0 | 0 |

Straiton (cont.)

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 27-S-1 | 4 | 4 | 0 | 0 | 4 | 0 | 0 | 0 |
| 31-S-1 | 3 | 8 | 0 | 0 | 3 | 0 | 0 | 0 |
| 1-S-2 | NA | NA | NA | NA | NA | NA | NA | NA |
| 2-S-2 | NA | NA | NA | NA | NA | NA | NA | NA |
| 4-S-2 | NA | NA | NA | NA | NA | NA | NA | NA |
| 5-S-2 | NA | NA | NA | NA | NA | NA | NA | NA |
| 7-S-2 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 |
| 8-S-2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| 10-S-2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11-S-2 | 0 | 4 | 0 | 2 | 3 | 1 | 0 | 0 |
| 12-S-2 | 0 | 3 | 1 | 0 | 3 | 0 | 0 | 0 |
| 13-S-2 | 0 | 1 | 0 | 0 | 0 | 2 | 0 | 0 |
| 14-S-2 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 |
| 15-S-2 | 0 | 4 | 0 | 0 | 1 | 0 | 0 | 0 |
| 16-S-2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 |
| 18-S-2 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 19-S-2 | 0 | 13 | 0 | 0 | 6 | 0 | 0 | 0 |
| 20-S-2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21-S-2 | 10 | 3 | 0 | 0 | 3 | 0 | 0 | 0 |
| 22-S-2 | 11 | 7 | 0 | 0 | 8 | 2 | 0 | 0 |
| 23-S-2 | 1 | 2 | 0 | 0 | 2 | 2 | 0 | 0 |
| 24-S-2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| 25-S-2 | 0 | 7 | 0 | 1 | 1 | 0 | 1 | 0 |
| 26-S-2 | 6 | 7 | 0 | 0 | 4 | 0 | 0 | 0 |

Straiton (cont.)

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 28-S-2 | 3 | 10 | 0 | 0 | 4 | 0 | 0 | 0 |
| 29-S-2 | 5 | 1 | 0 | 0 | 1 | 3 | 0 | 0 |
| 30-S-2 | 1 | 4 | 0 | 2 | 3 | 4 | 0 | 0 |
| 31-S-2 | 5 | 5 | 0 | 3 | 3 | 1 | 0 | 0 |
| 32-S-2 | 9 | 7 | 0 | 2 | 6 | 0 | 0 | 0 |
| 33-S-2 | 3 | 2 | 0 | 2 | 4 | 3 | 0 | 0 |
| 34-S-2 | 4 | 3 | 0 | 1 | 3 | 1 | 0 | 0 |
| 35-S-2 | 2 | 1 | 0 | 0 | 4 | 0 | 1 | 0 |
| 36-S-2 | 5 | 0 | 0 | 1 | 1 | 2 | 0 | 0 |
| 38-S-2 | 1 | 1 | 0 | 0 | 1 | 2 | 0 | 0 |
| 39-S-2 | 6 | 3 | 0 | 0 | 1 | 1 | 0 | 0 |

Hagshaw Hills

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 1-H-1 | 1 | 2 | 0 | 3 | 0 | 0 | 0 | 0 |
| 2-H-1 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 |
| 3-H-1 | 4 | 1 | 0 | 1 | 5 | 0 | 0 | 1 |
| 4-H-1 | 7 | 2 | 0 | 2 | 11 | 0 | 2 | 0 |
| 5-H-1 | 8 | 0 | 0 | 0 | 4 | 1 | 0 | 0 |
| 6-H-1 | 25 | 4 | 0 | 0 | 1 | 16 | 1 | 1 |
| 7-H-1 | 1 | 1 | 0 | 1 | 1 | 3 | 0 | 0 |
| 9-H-1 | 2 | 10 | 0 | 1 | 1 | 0 | 0 | 0 |
| 10-H-1 | 5 | 1 | 0 | 4 | 5 | 14 | 0 | 0 |
| 11-H-1 | 7 | 1 | 0 | 2 | 1 | 4 | 0 | 0 |
| 12-H-1 | 8 | 0 | 0 | 0 | 4 | 5 | 0 | 0 |
| 14-H-1 | 14 | 5 | 0 | 0 | 8 | 5 | 1 | 0 |
| 15-H-1 | 22 | 3 | 0 | 0 | 6 | 10 | 0 | 0 |
| 16-H-1 | 14 | 4 | 0 | 1 | 2 | 0 | 0 | 1 |
| 17-H-1 | 15 | 0 | 0 | 1 | 2 | 6 | 0 | 0 |
| 18-H-1 | 6 | 1 | 0 | 3 | 5 | 2 | 1 | 0 |
| 19-H-1 | 4 | 3 | 0 | 2 | 3 | 0 | 0 | 0 |
| 20-H-1 | 7 | 0 | 0 | 0 | 1 | 6 | 0 | 1 |
| 21-H-1 | 12 | 1 | 0 | 1 | 1 | 2 | 0 | 0 |
| 1-H-3 | 14 | 2 | 0 | 4 | 6 | 2 | 0 | 0 |
| 2-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 3-H-3 | 18 | 3 | 1 | 0 | 2 | 0 | 0 | 1 |
| 4-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 5-H-3 | 9 | 1 | 0 | 3 | 1 | 7 | 0 | 0 |

Hagsshaw Hills (cont.)

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 6-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 11-H-3 | 2 | 0 | 0 | 3 | 2 | 9 | 0 | 0 |
| 12-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 13-H-3 | 9 | 1 | 0 | 0 | 4 | 7 | 2 | 2 |
| 14-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 15-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 17-H-3 | 28 | 4 | 0 | 1 | 8 | 6 | 1 | 0 |
| 18-H-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 19-H-3 | 21 | 4 | 0 | 1 | 3 | 7 | 1 | 1 |
| 1-H-4 | NA | NA | NA | NA | NA | NA | NA | NA |
| 2-H-4 | NA | NA | NA | NA | NA | NA | NA | NA |
| 3-H-4 | NA | NA | NA | NA | NA | NA | NA | NA |

Tinto-Carmichael

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 3-T-1 | 5 | 3 | 98 | 3 | 3 | 18 | 0 | 0 |
| 4-T-1 | 2 | 2 | 0 | 3 | 7 | 10 | 0 | 2 |
| 5-T-1 | 3 | 1 | 0 | 0 | 4 | 5 | 0 | 0 |
| 6-T-1 | 3 | 1 | 66 | 2 | 2 | 4 | 0 | 1 |
| 7-T-1 | 0 | 1 | 28 | 2 | 2 | 3 | 0 | 1 |
| 8-T-1 | 1 | 1 | 24 | 1 | 1 | 3 | 0 | 0 |
| 9-T-1 | 4 | 3 | 66 | 0 | 2 | 5 | 0 | 14 |
| 10-T-1 | 0 | 3 | 1 | 0 | 1 | 10 | 0 | 18 |
| 11-T-1 | 1 | 2 | 163 | 1 | 2 | 8 | 0 | 10 |
| 12-T-1 | 2 | 0 | 74 | 3 | 0 | 1 | 0 | 17 |
| 13-T-1 | 4 | 0 | 44 | 0 | 3 | 7 | 0 | 7 |
| 14-T-1 | 1 | 5 | 113 | 1 | 1 | 1 | 0 | 1 |
| 16-T-1 | 2 | 4 | 12 | 4 | 3 | 9 | 0 | 0 |
| 17-T-1 | 1 | 0 | 47 | 2 | 0 | 3 | 0 | 0 |
| 1-C-1 | 6 | 2 | 74 | 4 | 1 | 8 | 0 | 0 |
| 2-C-1 | 0 | 0 | 5 | 0 | 1 | 1 | 0 | 1 |
| 3-C-1 | 5 | 12 | 171 | 0 | 3 | 0 | 0 | 0 |
| 4-C-1 | 4 | 3 | 137 | 1 | 4 | 4 | 1 | 23 |
| 5-C-1 | 1 | 0 | 99 | 0 | 0 | 0 | 0 | 1 |
| 6-C-1 | 1 | 1 | 0 | 2 | 2 | 0 | 0 | 0 |
| 7-C-1 | 0 | 0 | 90 | 3 | 0 | 5 | 0 | 4 |

North Esk

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|---------|---------|------|---------|---------|--------|--------|--------|--------|
| 1-NE-1 | 1 | 1 | 94 | 0 | 2 | 6 | 0 | 14 |
| 2-NE-1 | 5 | 4 | 100 | 4 | 2 | 1 | 0 | 7 |
| 3-NE-1 | 2 | 1 | 81 | 1 | 0 | 14 | 0 | 13 |
| 4-NE-1 | 2 | 3 | 108 | 0 | 1 | 5 | 0 | 18 |
| 5-NE-1 | 4 | 2 | 39 | 2 | 0 | 6 | 0 | 4 |
| 7-NE-1 | 5 | 1 | 15 | 1 | 0 | 2 | 0 | 12 |
| 8-NE-1 | 2 | 1 | 54 | 0 | 0 | 1 | 0 | 5 |
| 9-NE-1 | 1 | 2 | 13 | 2 | 0 | 3 | 0 | 5 |
| 10-NE-1 | 2 | 2 | 89 | 2 | 0 | 5 | 0 | 9 |
| 11-NE-1 | 2 | 0 | 105 | 0 | 0 | 1 | 0 | 5 |
| 12-NE-1 | 4 | 0 | 16 | 1 | 0 | 0 | 0 | 1 |
| 13-NE-1 | 2 | 1 | 11 | 0 | 0 | 0 | 0 | 1 |
| 14-NE-1 | 6 | 2 | 34 | 0 | 4 | 6 | 0 | 6 |
| 15-NE-1 | 3 | 1 | 14 | 1 | 0 | 0 | 0 | 2 |
| 16-NE-1 | 8 | 2 | 5 | 0 | 2 | 4 | 0 | 1 |
| 17-NE-1 | 3 | 1 | 14 | 0 | 0 | 6 | 0 | 0 |
| 18-NE-1 | 8 | 3 | 11 | 0 | 0 | 4 | 0 | 2 |
| 19-NE-1 | 4 | 0 | 43 | 1 | 0 | 11 | 0 | 4 |
| 20-NE-1 | 4 | 0 | 2 | 0 | 1 | 1 | 0 | 3 |
| 21-NE-1 | 1 | 0 | 2 | 1 | 1 | 0 | 0 | 2 |
| 22-NE-1 | 7 | 1 | 83 | 1 | 1 | 0 | 0 | 10 |
| 23-NE-1 | 2 | 3 | 15 | 1 | 2 | 11 | 0 | 0 |
| 24-NE-1 | 4 | 1 | 94 | 1 | 1 | 4 | 0 | 1 |
| 25-NE-1 | 2 | 1 | 48 | 0 | 1 | 8 | 0 | 2 |

North Esk (cont.)

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|---------|---------|------|---------|---------|--------|--------|--------|--------|
| 1-NE-2 | 0 | 0 | 0 | 2 | 0 | 2 | 0 | 0 |
| 2-NE-2 | 1 | 8 | 3 | 0 | 6 | 1 | 0 | 3 |
| 3-NE-2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| 4-NE-2 | 1 | 0 | 1 | 7 | 3 | 6 | 0 | 1 |
| 5-NE-2 | 0 | 4 | 1 | 2 | 4 | 2 | 0 | 3 |
| 6-NE-2 | 0 | 2 | 13 | 0 | 4 | 8 | 0 | 1 |
| 9-NE-2 | 2 | 5 | 1 | 2 | 2 | 10 | 0 | 1 |
| 10-NE-2 | 0 | 1 | 0 | 1 | 3 | 1 | 0 | 0 |
| 11-NE-2 | 2 | 2 | 0 | 2 | 7 | 4 | 0 | 0 |
| 12-NE-2 | 4 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| 13-NE-2 | 2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 |
| 15-NE-2 | 4 | 7 | 1 | 0 | 5 | 7 | 0 | 2 |
| 17-NE-2 | 2 | 4 | 0 | 1 | 2 | 2 | 0 | 1 |
| 18-NE-2 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| 19-NE-2 | 4 | 2 | 1 | 0 | 2 | 0 | 0 | 0 |
| 21-NE-2 | 1 | 2 | 0 | 2 | 1 | 5 | 0 | 0 |
| 22-NE-2 | 2 | 2 | 1 | 5 | 1 | 8 | 0 | 0 |
| 23-NE-2 | 1 | 3 | 0 | 1 | 5 | 6 | 0 | 1 |
| 24-NE-2 | 4 | 1 | 73 | 0 | 2 | 2 | 0 | 5 |
| 25-NE-2 | 1 | 4 | 3 | 1 | 2 | 15 | 0 | 2 |
| 26-NE-2 | 5 | 4 | 3 | 1 | 6 | 1 | 1 | 1 |
| 1-NE-3 | NA | NA | NA | NA | NA | NA | NA | NA |
| 2-NE-3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1-NE-4 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 2 |

North Esk (cont.)

| Sample | Apatite | tour | epidote | ver.chl | zircon | garnet | rutile | sphene |
|--------|---------|------|---------|---------|--------|--------|--------|--------|
| 2-NE-4 | 3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4-NE-4 | 1 | 1 | 0 | 0 | 0 | 5 | 0 | 0 |
| 5-NE-4 | 5 | 4 | 5 | 0 | 0 | 15 | 0 | 1 |
| 6-NE-4 | 3 | 4 | 4 | 0 | 0 | 5 | 0 | 2 |
| 7-NE-4 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| 1-NE-5 | 0 | 5 | 2 | 0 | 5 | 5 | 0 | 1 |
| 2-NE-5 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 |
| 3-NE-5 | 5 | 2 | 2 | 1 | 0 | 7 | 0 | 0 |

| <i>Sample</i> | 1s1 | 1s1* | 2s1 | 2s1* | 3s1 | 3s1* | 4s1 | 4s1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 82.06 | 83.03 | 81.94 | 83.63 | 78.27 | 82.27 | 83.55 | 83.59 |
| TiO ₂ | 0.76 | 0.77 | 0.80 | 0.82 | 0.62 | 0.65 | 0.75 | 0.75 |
| Al ₂ O ₃ | 9.04 | 9.15 | 9.03 | 9.22 | 8.65 | 9.09 | 8.88 | 8.88 |
| Fe ₂ O ₃ | 0.95 | 0.96 | 0.73 | 0.75 | 0.60 | 0.63 | 0.90 | 0.90 |
| Feo | 0.41 | 0.41 | 0.52 | 0.53 | 0.86 | 0.90 | 0.21 | 0.21 |
| MnO | 0.04 | 0.04 | 0.02 | 0.02 | 0.06 | 0.06 | 0.07 | 0.07 |
| MgO | 0.53 | 0.54 | 0.48 | 0.49 | 0.96 | 1.01 | 0.56 | 0.56 |
| CaO | 0.85 | 0.00 | 1.97 | 0.00 | 3.04 | 0.00 | 0.66 | 0.00 |
| Na ₂ O | 0.52 | 0.53 | 0.09 | 0.09 | 0.26 | 0.27 | 0.94 | 0.94 |
| K ₂ O | 1.33 | 1.35 | 1.00 | 1.02 | 1.25 | 1.31 | 1.28 | 1.28 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.19 | 0.19 | 0.13 | 0.14 | 0.13 | 0.13 |
| H ₂ O+ | 2.92 | 2.95 | 2.84 | 2.90 | 2.85 | 3.00 | 2.51 | 2.51 |
| CO ₂ | 0.71 | 0.15 | 1.64 | 0.35 | 2.99 | 0.66 | 0.81 | 0.17 |
| Total | 100.24 | | 101.25 | | 100.54 | | 101.25 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 316 | | 236 | | 248 | | 264 | |
| ce | 19 | | 48 | | 21 | | 34 | |
| co | 7 | | 8 | | 9 | | 3 | |
| cr | 48 | | 56 | | 41 | | 43 | |
| cu | 10 | | 4 | | 7 | | 2 | |
| ga | 10 | | 9 | | 9 | | 8 | |
| la | 2 | | 21 | | 8 | | 16 | |
| ni | 20 | | 21 | | 20 | | 9 | |
| pb | 12 | | 8 | | 8 | | 14 | |
| rb | 43 | | 34 | | 42 | | 41 | |
| sr | 34 | | 36 | | 41 | | 29 | |
| th | 6 | | 8 | | 6 | | 8 | |
| u | 3 | | 4 | | 2 | | 2 | |
| y | 14 | | 24 | | 17 | | 13 | |
| zn | 31 | | 29 | | 21 | | 23 | |
| zr | 208 | | 368 | | 158 | | 216 | |
| rb | 19 | | 18 | | 19 | | 16 | |

| <i>Sample</i> | 5s1 | 5s1* | 6s1 | 6s1* | 7s1 | 7s1* | 8s1 | 8s1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 58.35 | 75.84 | 79.69 | 82.13 | 77.12 | 80.34 | 84.06 | 85.61 |
| TiO ₂ | 0.59 | 0.77 | 0.81 | 0.83 | 0.78 | 0.81 | 0.66 | 0.67 |
| Al ₂ O ₃ | 8.15 | 10.59 | 8.25 | 8.50 | 10.16 | 10.58 | 6.58 | 6.70 |
| Fe ₂ O ₃ | 2.42 | 3.15 | 2.34 | 2.41 | 1.06 | 1.10 | 1.07 | 1.09 |
| FeO | 1.60 | 2.08 | 0.25 | 0.26 | 0.62 | 0.65 | 0.79 | 0.80 |
| MnO | 0.09 | 0.12 | 0.07 | 0.07 | 0.08 | 0.08 | 0.05 | 0.05 |
| MgO | 1.13 | 1.47 | 0.67 | 0.69 | 0.63 | 0.66 | 0.73 | 0.74 |
| CaO | 13.69 | 0.49 | 2.19 | 0.18 | 2.64 | 0.12 | 1.43 | 0.00 |
| Na ₂ O | 0.22 | 0.29 | 0.75 | 0.77 | 0.26 | 0.27 | 0.55 | 0.56 |
| K ₂ O | 1.01 | 1.31 | 1.42 | 1.46 | 1.80 | 1.88 | 1.00 | 1.02 |
| P ₂ O ₅ | 0.13 | 0.17 | 0.13 | 0.13 | 0.16 | 0.17 | 0.05 | 0.05 |
| H ₂ O | 2.87 | 3.73 | 2.48 | 2.56 | 3.21 | 3.34 | 2.26 | 2.30 |
| CO ₂ | 10.48 | 0.00 | 1.59 | 0.00 | 1.99 | 0.00 | 1.85 | 0.40 |
| Total | 100.73 | | 100.64 | | 100.51 | | 101.08 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 158 | | 321 | | 391 | | 262 | |
| ce | 65 | | 48 | | 43 | | 38 | |
| co | 11 | | 7 | | 4 | | 6 | |
| cr | 141 | | 54 | | 54 | | 36 | |
| cu | 31 | | 12 | | 1 | | 20 | |
| ga | 7 | | 9 | | 10 | | 8 | |
| la | 30 | | 19 | | 17 | | 13 | |
| ni | 42 | | 23 | | 11 | | 23 | |
| pb | 8 | | 6 | | 7 | | 4 | |
| rb | 30 | | 45 | | 59 | | 29 | |
| sr | 105 | | 37 | | 46 | | 39 | |
| th | 7 | | 6 | | 7 | | 5 | |
| u | 2 | | 3 | | 3 | | 2 | |
| y | 26 | | 22 | | 22 | | 17 | |
| zn | 46 | | 38 | | 26 | | 32 | |
| zr | 227 | | 265 | | 197 | | 182 | |
| rb | 9 | | 15 | | 21 | | 10 | |

| <i>Sample</i> | 9s1 | 9s1* | 10s1 | 10s1* | 11s1 | 11s1* | 12s1 | 12s1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 78.66 | 82.47 | 76.60 | 80.03 | 76.72 | 78.47 | 85.37 | 87.86 |
| TiO ₂ | 0.76 | 0.80 | 0.77 | 0.80 | 0.93 | 0.95 | 0.51 | 0.52 |
| Al ₂ O ₃ | 8.55 | 8.96 | 8.47 | 8.85 | 10.74 | 10.99 | 5.55 | 5.71 |
| Fe ₂ O ₃ | 1.77 | 1.86 | 0.88 | 0.92 | 1.30 | 1.33 | 0.95 | 0.98 |
| FeO | 0.61 | 0.64 | 1.83 | 1.91 | 1.04 | 1.06 | 0.64 | 0.66 |
| MnO | 0.05 | 0.05 | 0.07 | 0.07 | 0.04 | 0.04 | 0.06 | 0.06 |
| MgO | 0.44 | 0.46 | 1.70 | 1.78 | 0.98 | 1.00 | 0.86 | 0.89 |
| CaO | 3.33 | 0.27 | 2.27 | 0.00 | 1.76 | 0.00 | 1.40 | 0.00 |
| Na ₂ O | 0.63 | 0.66 | 1.14 | 1.19 | 1.35 | 1.38 | 0.60 | 0.62 |
| K ₂ O | 0.96 | 1.01 | 1.41 | 1.47 | 1.73 | 1.77 | 0.77 | 0.79 |
| P ₂ O ₅ | 0.21 | 0.22 | 0.41 | 0.43 | 0.18 | 0.18 | 0.05 | 0.05 |
| H ₂ O+ | 2.48 | 2.60 | 1.80 | 1.88 | 2.37 | 2.42 | 1.48 | 1.52 |
| CO ₂ | 2.42 | 0.00 | 3.02 | 0.66 | 1.85 | 0.40 | 1.55 | 0.33 |
| Total | 100.87 | | 100.37 | | 100.99 | | 99.79 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 225 | | 240 | | 298 | | 126 | |
| ce | 74 | | 36 | | 59 | | 25 | |
| co | 3 | | 2 | | 4 | | 0 | |
| cr | 77 | | 62 | | 57 | | 40 | |
| cu | 11 | | 13 | | 7 | | 4 | |
| ga | 8 | | 10 | | 11 | | 6 | |
| la | 31 | | 13 | | 24 | | 10 | |
| ni | 28 | | 15 | | 20 | | 10 | |
| pb | 6 | | 6 | | 7 | | 5 | |
| rb | 31 | | 46 | | 55 | | 25 | |
| sr | 49 | | 48 | | 55 | | 30 | |
| th | 7 | | 8 | | 8 | | 5 | |
| u | 2 | | 3 | | 2 | | 3 | |
| y | 31 | | 21 | | 29 | | 15 | |
| zn | 41 | | 32 | | 34 | | 20 | |
| zr | 315 | | 237 | | 366 | | 176 | |
| nb | 19 | | 18 | | 19 | | 6 | |

| <i>Sample</i> | 13s1 | 13s1* | 14s1 | 14s1* | 15s1 | 15s1* | 16s1 | 16s1* |
|--------------------------------|--------|-------|-------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 73.81 | 77.59 | 80.15 | 83.69 | 81.48 | 84.64 | 81.93 | 83.78 |
| TiO ₂ | 0.88 | 0.93 | 0.85 | 0.89 | 0.79 | 0.82 | 0.62 | 0.63 |
| Al ₂ O ₃ | 10.59 | 11.13 | 7.38 | 7.71 | 6.88 | 7.15 | 8.17 | 8.35 |
| Fe ₂ O ₃ | 1.89 | 1.99 | 0.70 | 0.73 | 0.54 | 0.56 | 0.65 | 0.66 |
| FeO | 0.99 | 1.04 | 1.05 | 1.10 | 1.28 | 1.33 | 0.91 | 0.93 |
| MnO | 0.09 | 0.09 | 0.06 | 0.06 | 0.06 | 0.06 | 0.07 | 0.07 |
| MgO | 0.90 | 0.95 | 1.14 | 1.19 | 1.23 | 1.28 | 0.97 | 0.99 |
| CaO | 3.11 | 0.25 | 1.94 | 0.00 | 1.65 | 0.00 | 1.50 | 0.00 |
| Na ₂ O | 1.14 | 1.20 | 1.13 | 1.18 | 1.09 | 1.13 | 0.25 | 0.26 |
| K ₂ O | 1.79 | 1.88 | 1.08 | 1.13 | 0.98 | 1.02 | 1.18 | 1.21 |
| P ₂ O ₅ | 0.14 | 0.15 | 0.18 | 0.19 | 0.15 | 0.16 | 0.12 | 0.12 |
| H ₂ O | 2.67 | 2.81 | 1.56 | 1.63 | 1.39 | 1.44 | 2.48 | 2.54 |
| CO ₂ | 2.26 | 0.00 | 2.35 | 0.52 | 1.87 | 0.41 | 2.11 | 0.45 |
| Total | 100.26 | | 99.57 | | 99.39 | | 100.96 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 394 | | 174 | | 169 | | 263 | |
| ce | 34 | | 41 | | 47 | | 57 | |
| co | 6 | | 0 | | 1 | | 10 | |
| cr | 104 | | 53 | | 43 | | 55 | |
| cu | 16 | | 7 | | 5 | | 8 | |
| ga | 12 | | 7 | | 6 | | 8 | |
| la | 14 | | 17 | | 18 | | 22 | |
| ni | 20 | | 10 | | 11 | | 22 | |
| pb | 6 | | 5 | | 7 | | 10 | |
| rb | 59 | | 35 | | 32 | | 40 | |
| sr | 51 | | 46 | | 41 | | 81 | |
| th | 7 | | 8 | | 4 | | 6 | |
| u | 2 | | 3 | | 3 | | 3 | |
| y | 23 | | 24 | | 20 | | 20 | |
| zn | 39 | | 28 | | 27 | | 29 | |
| zr | 259 | | 322 | | 290 | | 141 | |
| rb | 15 | | 16 | | 14 | | 15 | |

| <i>Sample</i> | 17s1 | 17s1* | 18s1 | 18s1* | 19s1 | 19s1* | 20s1 | 20s1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.76 | 82.59 | 81.21 | 83.26 | 80.24 | 85.44 | 79.54 | 85.24 |
| TiO ₂ | 0.82 | 0.84 | 0.72 | 0.74 | 0.50 | 0.53 | 0.48 | 0.51 |
| Al ₂ O ₃ | 9.64 | 9.86 | 9.06 | 9.29 | 5.47 | 5.82 | 5.65 | 6.05 |
| Fe ₂ O ₃ | 0.54 | 0.55 | 0.70 | 0.72 | 0.39 | 0.42 | 0.61 | 0.65 |
| FeO | 0.65 | 0.66 | 0.76 | 0.78 | 1.60 | 1.70 | 1.50 | 1.61 |
| MnO | 0.04 | 0.04 | 0.03 | 0.03 | 0.08 | 0.09 | 0.09 | 0.10 |
| MgO | 0.84 | 0.86 | 0.89 | 0.91 | 1.63 | 1.74 | 1.79 | 1.92 |
| CaO | 1.44 | 0.00 | 1.88 | 0.00 | 3.30 | 0.00 | 3.48 | 0.00 |
| Na ₂ O | 0.01 | 0.01 | 0.00 | 0.00 | 0.34 | 0.36 | 0.00 | 0.00 |
| K ₂ O | 1.34 | 1.37 | 1.21 | 1.24 | 0.83 | 0.88 | 0.85 | 0.91 |
| P ₂ O ₅ | 0.16 | 0.16 | 0.14 | 0.14 | 0.08 | 0.09 | 0.08 | 0.09 |
| H ₂ O | 2.59 | 2.65 | 2.31 | 2.37 | 1.82 | 1.94 | 1.75 | 1.88 |
| CO ₂ | 1.87 | 0.40 | 2.43 | 0.52 | 4.47 | 1.00 | 4.64 | 1.04 |
| Total | 100.70 | | 101.34 | | 100.75 | | 100.46 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 301 | | 250 | | 128 | | 125 | |
| ce | 78 | | 46 | | 38 | | 38 | |
| co | 13 | | 21 | | 4 | | 4 | |
| cr | 117 | | 59 | | 42 | | 32 | |
| cu | 7 | | 8 | | 3 | | 3 | |
| ga | 10 | | 10 | | 6 | | 7 | |
| la | 30 | | 18 | | 21 | | 16 | |
| ni | 18 | | 26 | | 14 | | 14 | |
| pb | 8 | | 12 | | 8 | | 4 | |
| rb | 48 | | 42 | | 28 | | 29 | |
| sr | 67 | | 56 | | 37 | | 41 | |
| th | 8 | | 4 | | 6 | | 7 | |
| u | 5 | | 4 | | 2 | | 3 | |
| y | 25 | | 22 | | 15 | | 16 | |
| zn | 771 | | 27 | | 27 | | 24 | |
| zr | 312 | | 265 | | 158 | | 137 | |
| rb | 21 | | 16 | | 10 | | 12 | |

| <i>Sample</i> | 21s1 | 21s1* | 22s1 | 22s1* | 23s1 | 23s1* | 24s1 | 24s1* |
|--------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 78.98 | 81.34 | 79.30 | 83.45 | 78.59 | 81.73 | 78.92 | 81.71 |
| TiO ₂ | 0.72 | 0.74 | 0.52 | 0.55 | 0.72 | 0.75 | 0.72 | 0.75 |
| Al ₂ O ₃ | 9.21 | 9.49 | 7.76 | 8.17 | 9.37 | 9.74 | 9.40 | 9.73 |
| Fe ₂ O ₃ | 1.18 | 1.22 | 1.00 | 1.05 | 0.58 | 0.60 | 0.58 | 0.60 |
| FeO | 1.41 | 1.45 | 1.14 | 1.20 | 1.14 | 1.19 | 1.08 | 1.12 |
| MnO | 0.03 | 0.03 | 0.08 | 0.08 | 0.06 | 0.06 | 0.04 | 0.04 |
| MgO | 1.12 | 1.15 | 1.24 | 1.30 | 1.21 | 1.26 | 1.22 | 1.26 |
| CaO | 2.08 | 0.00 | 2.22 | 0.00 | 2.17 | 0.00 | 1.94 | 0.00 |
| Na ₂ O | 0.14 | 0.14 | 0.18 | 0.19 | 0.00 | 0.00 | 0.07 | 0.07 |
| K ₂ O | 1.45 | 1.49 | 1.14 | 1.20 | 1.27 | 1.32 | 1.33 | 1.38 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.05 | 0.05 | 0.12 | 0.12 | 0.13 | 0.13 |
| H ₂ O | 2.13 | 2.19 | 1.92 | 2.02 | 2.50 | 2.60 | 2.56 | 2.65 |
| CO ₂ | 2.83 | 0.61 | 3.30 | 0.73 | 2.87 | 0.63 | 2.55 | 0.55 |
| Total | 101.41 | | 99.85 | | 100.60 | | 100.54 | |

| | | | | |
|--------------------------------|-----|-----|-----|-----|
| <i>trace elements (p.p.m.)</i> | | | | |
| ba | 228 | 213 | 215 | 233 |
| ce | 60 | 51 | 51 | 60 |
| co | 6 | 4 | 1 | 2 |
| cr | 48 | 37 | 52 | 40 |
| cu | 0 | 0 | 6 | 3 |
| ga | 9 | 9 | 10 | 9 |
| la | 22 | 24 | 20 | 22 |
| ni | 19 | 14 | 20 | 23 |
| pb | 4 | 4 | 4 | 5 |
| rb | 50 | 42 | 45 | 48 |
| sr | 45 | 51 | 36 | 35 |
| th | 8 | 6 | 6 | 8 |
| u | 3 | 3 | 3 | 4 |
| y | 23 | 17 | 25 | 26 |
| zn | 34 | 36 | 28 | 31 |
| zr | 255 | 148 | 248 | 248 |
| rb | 13 | 9 | 18 | 17 |

| <i>Sample</i> | 25s1 | 25s1* | 26s1 | 26s1* | 27s1 | 27s1* | 28s1 | 28s1* |
|--------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 82.65 | 83.68 | 77.67 | 79.23 | 79.72 | 82.15 | 80.19 | 80.58 |
| TiO ₂ | 0.79 | 0.80 | 0.93 | 0.95 | 0.70 | 0.72 | 0.79 | 0.79 |
| Al ₂ O ₃ | 8.92 | 9.03 | 9.56 | 9.75 | 9.97 | 10.27 | 9.27 | 9.31 |
| Fe ₂ O ₃ | 0.99 | 1.00 | 0.76 | 0.78 | 0.85 | 0.88 | 0.81 | 0.81 |
| FeO | 0.52 | 0.53 | 2.66 | 2.71 | 1.22 | 1.26 | 2.56 | 2.57 |
| MnO | 0.04 | 0.04 | 0.03 | 0.03 | 0.02 | 0.02 | 0.03 | 0.03 |
| MgO | 0.51 | 0.52 | 1.48 | 1.51 | 0.98 | 1.01 | 1.39 | 1.40 |
| CaO | 1.30 | 0.00 | 0.97 | 0.00 | 1.68 | 0.00 | 1.13 | 0.00 |
| Na ₂ O | 0.16 | 0.16 | 0.84 | 0.86 | 0.36 | 0.37 | 1.12 | 1.13 |
| K ₂ O | 1.20 | 1.21 | 1.19 | 1.21 | 1.56 | 1.61 | 1.19 | 1.20 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.10 | 0.10 | 0.13 | 0.13 | 0.15 | 0.15 |
| H ₂ O | 2.59 | 2.62 | 2.57 | 2.62 | 1.12 | 1.15 | 1.80 | 1.81 |
| CO ₂ | 1.30 | 0.28 | 1.17 | 0.25 | 1.96 | 0.42 | 1.04 | 0.22 |
| Total | 101.10 | | 99.93 | | 100.27 | | 101.47 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 228 | | 252 | | 264 | | 247 | |
| ce | 30 | | 31 | | 54 | | 52 | |
| co | 4 | | 9 | | 4 | | 4 | |
| cr | 56 | | 70 | | 54 | | 56 | |
| cu | 8 | | 10 | | 1 | | 11 | |
| ga | 8 | | 10 | | 9 | | 11 | |
| la | 17 | | 10 | | 19 | | 20 | |
| ni | 17 | | 27 | | 23 | | 22 | |
| pb | 7 | | 8 | | 5 | | 7 | |
| rb | 42 | | 45 | | 56 | | 45 | |
| sr | 32 | | 47 | | 42 | | 53 | |
| th | 7 | | 8 | | 7 | | 8 | |
| u | 3 | | 3 | | 3 | | 3 | |
| y | 23 | | 14 | | 23 | | 24 | |
| zn | 33 | | 59 | | 30 | | 51 | |
| zr | 310 | | 306 | | 214 | | 340 | |
| rb | 20 | | 16 | | 19 | | 16 | |

| <i>Sample</i> | 29s1 | 29s1* | 30s1 | 30s1* | 31s1 | 31s1* | 32s1 | 32s1* |
|--------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 81.31 | 84.06 | 78.83 | 83.02 | 74.78 | 78.08 | 86.96 | 87.43 |
| TiO ₂ | 0.73 | 0.75 | 0.74 | 0.78 | 0.77 | 0.80 | 0.40 | 0.40 |
| Al ₂ O ₃ | 8.46 | 8.75 | 8.65 | 9.11 | 9.64 | 10.07 | 7.15 | 7.19 |
| Fe ₂ O ₃ | 0.49 | 0.51 | 0.46 | 0.48 | 0.76 | 0.79 | 0.23 | 0.23 |
| FeO | 0.46 | 0.48 | 0.67 | 0.71 | 2.73 | 2.85 | 0.30 | 0.30 |
| MnO | 0.06 | 0.06 | 0.03 | 0.03 | 0.05 | 0.05 | 0.01 | 0.01 |
| MgO | 0.75 | 0.78 | 0.85 | 0.90 | 1.55 | 1.62 | 0.37 | 0.37 |
| CaO | 1.89 | 0.00 | 2.18 | 0.00 | 2.81 | 0.00 | 0.90 | 0.00 |
| Na ₂ O | 1.34 | 1.39 | 1.32 | 1.39 | 1.42 | 1.48 | 1.78 | 1.79 |
| K ₂ O | 1.39 | 1.44 | 1.02 | 1.07 | 1.29 | 1.35 | 0.69 | 0.69 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.12 | 0.13 | 0.14 | 0.15 | 0.09 | 0.09 |
| H ₂ O+ | 1.24 | 1.28 | 1.69 | 1.78 | 2.03 | 2.12 | 1.26 | 1.27 |
| CO ₂ | 1.80 | 0.39 | 2.75 | 0.61 | 2.93 | 0.64 | 1.06 | 0.22 |
| Total | 100.04 | | 99.31 | | 100.90 | | 101.20 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 248 | | 250 | | 284 | | 110 | |
| ce | 28 | | 27 | | 39 | | 19 | |
| co | 1 | | 0 | | 8 | | 1 | |
| cr | 80 | | 79 | | 42 | | 37 | |
| cu | 12 | | 23 | | 9 | | 5 | |
| ga | 8 | | 7 | | 10 | | 6 | |
| la | NA | | NA | | 14 | | 2 | |
| ni | 2 | | 9 | | 21 | | 4 | |
| pb | 4 | | 7 | | 6 | | 3 | |
| rb | 49 | | 37 | | 47 | | 20 | |
| sr | 70 | | 59 | | 69 | | 48 | |
| th | 4 | | 7 | | 7 | | 2 | |
| u | 2 | | 4 | | 4 | | 2 | |
| y | 16 | | 19 | | 24 | | 7 | |
| zn | 268 | | 24 | | 49 | | 15 | |
| zr | 220 | | 297 | | 259 | | 93 | |
| rb | 19 | | 8 | | 15 | | 10 | |

| <i>Sample</i> | 1s2 | 1s2* | 2s2 | 2s2* | 3s2 | 3s2* | 4s2 | 4s2* |
|--------------------------------|-------|-------|-------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 74.70 | 78.37 | 59.26 | 69.46 | 73.55 | 78.82 | 61.41 | 71.93 |
| TiO ₂ | 0.75 | 0.79 | 0.63 | 0.74 | 0.73 | 0.78 | 0.70 | 0.82 |
| Al ₂ O ₃ | 9.99 | 10.48 | 9.72 | 11.39 | 8.03 | 8.61 | 8.31 | 9.73 |
| Fe ₂ O ₃ | 1.77 | 1.86 | 1.96 | 2.30 | 1.08 | 1.16 | 1.78 | 2.08 |
| FeO | 2.44 | 2.56 | 2.81 | 3.29 | 1.96 | 2.10 | 2.51 | 2.94 |
| MnO | 0.04 | 0.04 | 0.10 | 0.12 | 0.10 | 0.11 | 0.10 | 0.12 |
| MgO | 1.49 | 1.56 | 4.11 | 4.82 | 2.26 | 2.42 | 4.24 | 4.97 |
| CaO | 2.40 | 0.13 | 6.84 | 0.00 | 3.70 | 0.00 | 7.16 | 0.00 |
| Na ₂ O | 0.00 | 0.00 | 0.16 | 0.19 | 1.22 | 1.31 | 0.16 | 0.19 |
| K ₂ O | 1.43 | 1.50 | 1.21 | 1.42 | 1.28 | 1.37 | 1.00 | 1.17 |
| P ₂ O ₅ | 0.13 | 0.14 | 0.16 | 0.19 | 0.26 | 0.28 | 0.13 | 0.15 |
| H ₂ O+ | 2.45 | 2.57 | 3.12 | 3.66 | 2.09 | 2.24 | 2.96 | 3.47 |
| CO ₂ | 1.79 | 0.00 | 9.91 | 2.44 | 3.58 | 0.81 | 9.90 | 2.44 |
| Total | 99.38 | | 99.99 | | 99.84 | | 100.36 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 260 | | 218 | | 210 | | 189 | |
| ce | 22 | | 28 | | 34 | | 26 | |
| co | 8 | | 14 | | 8 | | 14 | |
| cr | 53 | | 101 | | 44 | | 65 | |
| cu | 27 | | 3 | | 4 | | 2 | |
| ga | 10 | | 10 | | 8 | | 7 | |
| la | 7 | | 12 | | 8 | | 8 | |
| ni | 25 | | 36 | | 25 | | 31 | |
| pb | 7 | | 3 | | 8 | | 4 | |
| rb | 49 | | 38 | | 39 | | 32 | |
| sr | 36 | | 48 | | 44 | | 43 | |
| th | 8 | | 4 | | 6 | | 5 | |
| u | 2 | | 3 | | 3 | | 3 | |
| y | 16 | | 23 | | 30 | | 21 | |
| zn | 55 | | 45 | | 45 | | 43 | |
| zr | 236 | | 175 | | 245 | | 232 | |
| nb | 15 | | 12 | | 14 | | 8 | |

| Sample | 5s2 | 5s2* | 6s2 | 6s2* | 7s2 | 7s2* | 8s2 | 8s2* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.05 | 79.16 | 68.12 | 78.99 | 72.65 | 73.16 | 67.67 | 75.25 |
| TiO ₂ | 0.78 | 0.77 | 0.57 | 0.66 | 0.83 | 0.84 | 0.53 | 0.59 |
| Al ₂ O ₃ | 9.22 | 9.12 | 7.97 | 9.24 | 11.74 | 11.82 | 9.98 | 11.10 |
| Fe ₂ O ₃ | 1.32 | 1.31 | 1.29 | 1.50 | 1.79 | 1.80 | 1.19 | 1.32 |
| FeO | 2.39 | 2.36 | 1.96 | 2.27 | 3.52 | 3.54 | 2.21 | 2.46 |
| MnO | 0.07 | 0.07 | 0.11 | 0.13 | 0.04 | 0.04 | 0.07 | 0.08 |
| MgO | 1.99 | 1.97 | 1.46 | 1.69 | 2.87 | 2.89 | 2.45 | 2.72 |
| CaO | 0.52 | 0.06 | 8.78 | 0.31 | 0.71 | 0.29 | 6.36 | 0.00 |
| Na ₂ O | 1.32 | 1.31 | 0.35 | 0.41 | 0.75 | 0.76 | 0.52 | 0.58 |
| K ₂ O | 1.41 | 1.39 | 1.26 | 1.46 | 1.52 | 1.53 | 1.61 | 1.79 |
| P ₂ O ₅ | 0.15 | 0.15 | 0.12 | 0.14 | 0.14 | 0.14 | 0.09 | 0.10 |
| H ₂ O+ | 2.36 | 2.33 | 2.76 | 3.20 | 3.16 | 3.18 | 2.56 | 2.85 |
| CO ₂ | 0.36 | 0.00 | 6.70 | 0.00 | 0.33 | 0.00 | 5.00 | 1.17 |
| Total | 101.94 | | 101.45 | | 100.05 | | 100.24 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 257 | | 232 | | 265 | | 278 | |
| ce | 15 | | 93 | | 17 | | 39 | |
| co | 8 | | 6 | | 16 | | 6 | |
| cr | 47 | | 54 | | 73 | | 84 | |
| cu | 6 | | 6 | | 9 | | 6 | |
| ga | 8 | | 6 | | 11 | | 10 | |
| la | 2 | | 27 | | 0 | | 6 | |
| ni | 23 | | 16 | | 28 | | 48 | |
| pb | 6 | | 10 | | 7 | | 9 | |
| rb | 48 | | 42 | | 49 | | 50 | |
| sr | 49 | | 205 | | 49 | | 82 | |
| th | 8 | | 7 | | 7 | | 5 | |
| u | 3 | | 3 | | 2 | | 1 | |
| y | 14 | | 27 | | 13 | | 19 | |
| zn | 54 | | 40 | | 63 | | 50 | |
| zr | 235 | | 206 | | 208 | | 134 | |
| rb | 12 | | 13 | | 13 | | 13 | |

Sample 9s2 9s2* 10s2 10s2* 11s2 11s2* 12s2 12s2*

chemical analyses (%)

| | | | | | | | | |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| SiO ₂ | 56.81 | 68.24 | 71.43 | 70.83 | 81.35 | 83.35 | 75.81 | 76.81 |
| TiO ₂ | 0.82 | 0.98 | 0.95 | 0.94 | 0.76 | 0.78 | 0.75 | 0.76 |
| Al ₂ O ₃ | 9.50 | 11.41 | 11.76 | 11.66 | 7.58 | 7.77 | 10.09 | 10.22 |
| Fe ₂ O ₃ | 2.73 | 3.28 | 2.76 | 2.74 | 1.15 | 1.18 | 1.68 | 1.70 |
| FeO | 3.13 | 3.76 | 3.28 | 3.25 | 1.97 | 2.02 | 2.84 | 2.88 |
| MnO | 0.11 | 0.13 | 0.08 | 0.08 | 0.04 | 0.04 | 0.04 | 0.04 |
| MgO | 2.87 | 3.45 | 3.04 | 3.01 | 1.32 | 1.35 | 2.32 | 2.35 |
| CaO | 10.39 | 0.00 | 0.69 | 0.28 | 2.00 | 0.21 | 0.91 | 0.00 |
| Na ₂ O | 0.67 | 0.80 | 1.10 | 1.09 | 0.92 | 0.94 | 1.27 | 1.29 |
| K ₂ O | 1.27 | 1.53 | 1.71 | 1.70 | 1.08 | 1.11 | 1.33 | 1.35 |
| P ₂ O ₅ | 0.16 | 0.19 | 0.13 | 0.13 | 0.15 | 0.15 | 0.10 | 0.10 |
| H ₂ O+ | 3.46 | 4.16 | 4.32 | 4.28 | 1.07 | 1.10 | 2.31 | 2.34 |
| CO ₂ | 8.22 | 2.07 | 0.32 | 0.00 | 1.41 | 0.00 | 0.76 | 0.16 |
| Total | 100.14 | | 101.57 | | 100.80 | | 100.21 | |

trace elements (p.p.m)

| | | | | |
|----|-----|-----|-----|-----|
| ba | 219 | 303 | 234 | 263 |
| ce | 74 | 13 | 52 | 27 |
| co | 15 | 15 | 2 | 10 |
| cr | 155 | 92 | 49 | 80 |
| cu | 12 | 22 | 7 | 8 |
| ga | 10 | 13 | 8 | 11 |
| la | 27 | 6 | 22 | 4 |
| ni | 40 | 40 | 14 | 27 |
| pb | 8 | 11 | 7 | 9 |
| rb | 38 | 54 | 34 | 45 |
| sr | 81 | 47 | 61 | 46 |
| th | 7 | 8 | 7 | 5 |
| u | 3 | 3 | 4 | 3 |
| y | 52 | 16 | 26 | 13 |
| zn | 61 | 73 | 41 | 58 |
| zr | 287 | 205 | 376 | 194 |
| rb | 11 | 14 | 14 | 16 |

| <i>Sample</i> | 13s2 | 13s2* | 14s2 | 14s2* | 15s2 | 15s2* | 16s2 | 16s2* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 76.03 | 76.30 | 76.63 | 77.51 | 78.56 | 78.81 | 75.10 | 75.31 |
| TiO ₂ | 0.71 | 0.71 | 0.72 | 0.73 | 0.69 | 0.69 | 0.87 | 0.87 |
| Al ₂ O ₃ | 10.24 | 10.28 | 10.37 | 10.49 | 9.56 | 9.59 | 11.12 | 11.15 |
| Fe ₂ O ₃ | 1.82 | 1.83 | 1.05 | 1.06 | 1.47 | 1.47 | 2.50 | 2.51 |
| FeO | 2.40 | 2.41 | 2.60 | 2.63 | 2.21 | 2.22 | 2.66 | 2.67 |
| MnO | 0.04 | 0.04 | 0.05 | 0.05 | 0.02 | 0.02 | 0.03 | 0.03 |
| MgO | 2.73 | 2.74 | 2.36 | 2.39 | 1.44 | 1.44 | 2.02 | 2.03 |
| CaO | 0.65 | 0.26 | 0.71 | 0.04 | 0.83 | 0.54 | 0.51 | 0.00 |
| Na ₂ O | 0.87 | 0.87 | 1.33 | 1.35 | 2.03 | 2.04 | 1.36 | 1.36 |
| K ₂ O | 1.72 | 1.73 | 1.22 | 1.23 | 1.28 | 1.28 | 1.32 | 1.32 |
| P ₂ O ₅ | 0.14 | 0.14 | 0.11 | 0.11 | 0.20 | 0.20 | 0.13 | 0.13 |
| H ₂ O+ | 2.69 | 2.70 | 2.39 | 2.42 | 1.69 | 1.70 | 2.53 | 2.54 |
| CO ₂ | 0.31 | 0.00 | 0.53 | 0.00 | 0.23 | 0.00 | 0.41 | 0.09 |
| Total | 100.35 | | 100.07 | | 100.21 | | 100.56 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 340 | | 206 | | 247 | | 282 | |
| ce | 10 | | 20 | | 61 | | 44 | |
| co | 12 | | 13 | | 7 | | 11 | |
| cr | 92 | | 140 | | 49 | | 80 | |
| cu | 23 | | 7 | | 9 | | 11 | |
| ga | 11 | | 11 | | 10 | | 11 | |
| la | 4 | | 2 | | 24 | | 11 | |
| ni | 38 | | 47 | | 24 | | 35 | |
| pb | 9 | | 6 | | 8 | | 10 | |
| rb | 53 | | 40 | | 44 | | 47 | |
| sr | 36 | | 47 | | 51 | | 46 | |
| th | 9 | | 7 | | 8 | | 8 | |
| u | 3 | | 3 | | 2 | | 3 | |
| y | 13 | | 17 | | 26 | | 17 | |
| zn | 58 | | 53 | | 46 | | 68 | |
| zr | 204 | | 228 | | 237 | | 263 | |
| nb | 16 | | 15 | | 15 | | 16 | |

| <i>Sample</i> | 17s2 | 17s2* | 18s2 | 18s2* | 19s2 | 19s2* | 20s2 | 20s2* |
|--------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 84.97 | 86.13 | 85.54 | 86.32 | 83.26 | 83.87 | 85.33 | 84.85 |
| TiO ₂ | 0.58 | 0.59 | 1.04 | 1.05 | 0.96 | 0.97 | 0.54 | 0.54 |
| Al ₂ O ₃ | 7.64 | 7.74 | 6.96 | 7.02 | 7.76 | 7.82 | 8.10 | 8.05 |
| Fe ₂ O ₃ | 0.82 | 0.83 | 0.99 | 1.00 | 1.02 | 1.03 | 0.69 | 0.69 |
| FeO | 0.79 | 0.80 | 0.63 | 0.64 | 0.99 | 1.00 | 0.74 | 0.74 |
| MnO | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 |
| MgO | 0.46 | 0.47 | 0.75 | 0.76 | 0.78 | 0.79 | 0.58 | 0.58 |
| CaO | 1.00 | 0.11 | 0.23 | 0.00 | 0.40 | 0.00 | 0.55 | 0.26 |
| Na ₂ O | 0.65 | 0.66 | 0.79 | 0.80 | 1.77 | 1.78 | 1.26 | 1.25 |
| K ₂ O | 0.90 | 0.91 | 0.89 | 0.90 | 1.06 | 1.07 | 1.13 | 1.12 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.11 | 0.11 | 0.18 | 0.18 | 0.13 | 0.13 |
| H ₂ O+ | 1.59 | 1.61 | 1.31 | 1.32 | 1.39 | 1.40 | 1.79 | 1.78 |
| CO ₂ | 0.70 | 0.00 | 0.34 | 0.07 | 0.41 | 0.09 | 0.23 | 0.00 |
| Total | 100.24 | | 99.59 | | 100.00 | | 101.09 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 180 | | 146 | | 199 | | 196 | |
| ce | 31 | | 66 | | 60 | | 39 | |
| co | 4 | | 0 | | 4 | | 3 | |
| cr | 39 | | 164 | | 37 | | 67 | |
| cu | 8 | | 23 | | 17 | | 7 | |
| ga | 7 | | 8 | | 7 | | 6 | |
| la | 11 | | 30 | | 24 | | 15 | |
| ni | 20 | | 13 | | 22 | | 16 | |
| pb | 3 | | 4 | | 5 | | 3 | |
| rb | 30 | | 30 | | 33 | | 37 | |
| sr | 36 | | 46 | | 49 | | 54 | |
| th | 6 | | 8 | | 7 | | 4 | |
| u | 3 | | 3 | | 2 | | 2 | |
| y | 17 | | 21 | | 23 | | 17 | |
| zn | 27 | | 30 | | 28 | | 23 | |
| zr | 257 | | 398 | | 440 | | 150 | |
| nb | 14 | | 18 | | 19 | | 15 | |

| <i>Sample</i> | 21s2 | 21s2* | 22s2 | 22s2* | 23s2 | 23s2* | 24s2 | 24s2* |
|--------------------------------|-------|-------|--------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 70.45 | 73.39 | 77.83 | 78.60 | 73.60 | 77.27 | 76.37 | 76.72 |
| TiO ₂ | 0.83 | 0.86 | 0.87 | 0.88 | 0.85 | 0.89 | 0.72 | 0.72 |
| Al ₂ O ₃ | 12.48 | 13.00 | 10.01 | 10.11 | 8.96 | 9.41 | 9.85 | 9.90 |
| Fe ₂ O ₃ | 1.31 | 1.36 | 1.21 | 1.22 | 1.73 | 1.82 | 1.71 | 1.72 |
| FeO | 2.95 | 3.07 | 2.35 | 2.37 | 2.67 | 2.80 | 3.02 | 3.03 |
| MnO | 0.05 | 0.05 | 0.02 | 0.02 | 0.06 | 0.06 | 0.06 | 0.06 |
| MgO | 1.95 | 2.03 | 1.26 | 1.27 | 1.84 | 1.93 | 2.17 | 2.18 |
| CaO | 1.79 | 0.09 | 1.19 | 0.25 | 2.64 | 0.22 | 0.99 | 0.00 |
| Na ₂ O | 0.91 | 0.95 | 1.15 | 1.16 | 1.22 | 1.28 | 0.96 | 0.96 |
| K ₂ O | 1.39 | 1.45 | 1.48 | 1.49 | 1.25 | 1.31 | 1.20 | 1.21 |
| P ₂ O ₅ | 0.14 | 0.15 | 0.17 | 0.17 | 0.11 | 0.12 | 0.12 | 0.12 |
| H ₂ O+ | 3.44 | 3.58 | 2.42 | 2.44 | 2.75 | 2.89 | 3.20 | 3.21 |
| CO ₂ | 1.34 | 0.00 | 0.74 | 0.00 | 1.91 | 0.00 | 0.78 | 0.16 |
| Total | 99.03 | | 100.70 | | 99.59 | | 101.15 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 285 | | 275 | | 223 | | 225 | |
| ce | 16 | | 59 | | 27 | | 38 | |
| co | 12 | | 4 | | 11 | | 11 | |
| cr | 90 | | 48 | | 77 | | 105 | |
| cu | 6 | | 11 | | 7 | | 9 | |
| ga | 13 | | 11 | | 8 | | 11 | |
| la | 6 | | 26 | | 7 | | 21 | |
| ni | 40 | | 20 | | 28 | | 48 | |
| pb | 8 | | 7 | | 9 | | 11 | |
| rb | 47 | | 53 | | 40 | | 39 | |
| sr | 51 | | 53 | | 56 | | 52 | |
| th | 9 | | 7 | | 8 | | 7 | |
| u | 3 | | 2 | | 2 | | 3 | |
| y | 17 | | 27 | | 16 | | 21 | |
| zn | 69 | | 53 | | 53 | | 62 | |
| zr | 203 | | 339 | | 192 | | 173 | |
| rb | 16 | | 17 | | 10 | | 13 | |

| <i>Sample</i> | 25s2 | 25s2* | 26s2 | 26s2* | 27s2 | 27s2* | 28s2 | 28s2* |
|--------------------------------|--------|-------|--------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 75.04 | 78.83 | 78.95 | 78.91 | 78.52 | 83.10 | 80.59 | 82.16 |
| TiO ₂ | 0.84 | 0.88 | 0.83 | 0.83 | 0.71 | 0.75 | 0.55 | 0.56 |
| Al ₂ O ₃ | 8.33 | 8.75 | 9.45 | 9.44 | 6.67 | 7.06 | 8.19 | 8.35 |
| Fe ₂ O ₃ | 1.52 | 1.60 | 1.29 | 1.29 | 0.91 | 0.96 | 0.96 | 0.98 |
| FeO | 2.48 | 2.61 | 2.68 | 2.68 | 2.23 | 2.36 | 2.27 | 2.31 |
| MnO | 0.07 | 0.07 | 0.03 | 0.03 | 0.05 | 0.05 | 0.04 | 0.04 |
| MgO | 1.90 | 2.00 | 1.55 | 1.55 | 1.51 | 1.60 | 1.18 | 1.20 |
| CaO | 3.38 | 0.11 | 0.94 | 0.17 | 2.90 | 0.04 | 1.85 | 0.09 |
| Na ₂ O | 0.56 | 0.59 | 1.48 | 1.48 | 0.83 | 0.88 | 1.56 | 1.59 |
| K ₂ O | 1.23 | 1.29 | 1.39 | 1.39 | 1.16 | 1.23 | 0.89 | 0.91 |
| P ₂ O ₅ | 0.16 | 0.17 | 0.15 | 0.15 | 0.12 | 0.13 | 0.13 | 0.13 |
| H ₂ O+ | 2.96 | 3.11 | 2.09 | 2.09 | 1.74 | 1.84 | 1.64 | 1.67 |
| CO ₂ | 2.58 | 0.00 | 0.61 | 0.00 | 2.25 | 0.00 | 1.39 | 0.00 |
| Total | 101.05 | | 101.44 | | 99.60 | | 101.24 | |

| | | | | |
|-------------------------------|-----|-----|-----|-----|
| <i>trace elements (p.p.m)</i> | | | | |
| ba | 265 | 231 | 233 | 281 |
| ce | 63 | 53 | 37 | 57 |
| co | 6 | 8 | 5 | 9 |
| cr | 46 | 33 | 73 | 57 |
| cu | 2 | 8 | 5 | 11 |
| ga | 8 | 8 | 7 | 10 |
| la | 21 | 22 | 13 | 27 |
| ni | 24 | 14 | 17 | 20 |
| pb | 7 | 4 | 5 | 4 |
| rb | 42 | 32 | 36 | 45 |
| sr | 70 | 68 | 55 | 57 |
| th | 5 | 6 | 6 | 6 |
| u | 3 | 3 | 3 | 1 |
| y | 31 | 21 | 19 | 24 |
| zn | 56 | 44 | 47 | 57 |
| zr | 274 | 186 | 278 | 343 |
| rb | 17 | 16 | 14 | 13 |

| <i>Sample</i> | 29s2 | 29s2* | 30s2 | 30s2* | 31s2 | 31s2* | 32s2 | 32s2* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 76.48 | 76.47 | 63.41 | 72.78 | 73.31 | 73.31 | 81.82 | 82.33 |
| TiO ₂ | 0.76 | 0.76 | 0.79 | 0.91 | 0.76 | 0.76 | 0.87 | 0.88 |
| Al ₂ O ₃ | 10.73 | 10.73 | 9.66 | 11.09 | 11.02 | 11.02 | 7.71 | 7.76 |
| Fe ₂ O ₃ | 1.28 | 1.28 | 2.15 | 2.47 | 1.24 | 1.24 | 0.83 | 0.84 |
| FeO | 3.12 | 3.12 | 2.60 | 2.98 | 4.00 | 4.00 | 2.14 | 2.15 |
| MnO | 0.03 | 0.03 | 0.09 | 0.10 | 0.05 | 0.05 | 0.03 | 0.03 |
| MgO | 2.45 | 2.45 | 2.17 | 2.49 | 3.04 | 3.04 | 1.28 | 1.29 |
| CaO | 0.72 | 0.11 | 8.60 | 0.00 | 0.74 | 0.00 | 1.49 | 0.41 |
| Na ₂ O | 1.36 | 1.36 | 0.82 | 0.94 | 1.80 | 1.80 | 1.85 | 1.86 |
| K ₂ O | 1.44 | 1.44 | 1.27 | 1.46 | 1.35 | 1.35 | 1.04 | 1.05 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.12 | 0.14 | 0.14 | 0.14 | 0.16 | 0.16 |
| H ₂ O+ | 2.14 | 2.14 | 2.61 | 3.00 | 3.15 | 3.15 | 1.24 | 1.25 |
| CO ₂ | 0.48 | 0.00 | 6.84 | 1.65 | 0.67 | 0.14 | 0.85 | 0.00 |
| Total | 101.10 | | 101.13 | | 101.27 | | 101.31 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 216 | | 274 | | 365 | | 222 | |
| ce | 41 | | 38 | | 21 | | 46 | |
| co | 4 | | 13 | | 18 | | 8 | |
| cr | 53 | | 73 | | 117 | | 46 | |
| cu | 12 | | 18 | | 10 | | 12 | |
| ga | 7 | | 10 | | 13 | | 8 | |
| la | 19 | | 15 | | 5 | | 19 | |
| ni | 19 | | 28 | | 55 | | 19 | |
| pb | 6 | | 10 | | 7 | | 5 | |
| rb | 33 | | 42 | | 41 | | 33 | |
| sr | 63 | | 71 | | 62 | | 64 | |
| th | 8 | | 7 | | 7 | | 8 | |
| u | 3 | | 3 | | 3 | | 4 | |
| y | 22 | | 28 | | 16 | | 23 | |
| zn | 42 | | 60 | | 82 | | 41 | |
| zr | 518 | | 205 | | 194 | | 518 | |
| nb | 17 | | 13 | | 14 | | 14 | |

| <i>Sample</i> | 33s2 | 33s2* | 34s2 | 34s2* | 35s2 | 35s2* | 36s2 | 36s2* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 81.68 | 81.46 | 79.31 | 80.37 | 74.52 | 74.20 | 76.08 | 80.71 |
| TiO ₂ | 0.62 | 0.62 | 0.88 | 0.89 | 0.75 | 0.75 | 0.64 | 0.68 |
| Al ₂ O ₃ | 8.51 | 8.49 | 8.27 | 8.38 | 11.47 | 11.42 | 8.51 | 9.03 |
| Fe ₂ O ₃ | 0.74 | 0.74 | 0.78 | 0.79 | 1.19 | 1.18 | 0.84 | 0.89 |
| FeO | 2.46 | 2.45 | 2.76 | 2.80 | 3.80 | 3.78 | 2.26 | 2.40 |
| MnO | 0.03 | 0.03 | 0.08 | 0.08 | 0.05 | 0.05 | 0.04 | 0.04 |
| MgO | 1.32 | 1.32 | 1.59 | 1.61 | 2.29 | 2.28 | 1.27 | 1.35 |
| CaO | 0.94 | 0.57 | 0.82 | 0.07 | 0.56 | 0.14 | 3.50 | 0.06 |
| Na ₂ O | 1.37 | 1.37 | 1.79 | 1.81 | 2.03 | 2.02 | 1.40 | 1.49 |
| K ₂ O | 1.32 | 1.32 | 1.31 | 1.33 | 1.32 | 1.31 | 1.39 | 1.47 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.12 | 0.12 | 0.13 | 0.13 | 0.11 | 0.12 |
| H ₂ O+ | 1.54 | 1.54 | 1.72 | 1.74 | 2.74 | 2.73 | 1.66 | 1.76 |
| CO ₂ | 0.29 | 0.00 | 0.59 | 0.00 | 0.33 | 0.00 | 2.71 | 0.00 |
| Total | 100.93 | | 100.02 | | 101.18 | | 100.41 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 279 | | 265 | | 313 | | 287 | |
| ce | 33 | | 52 | | 38 | | 43 | |
| co | 2 | | 10 | | 14 | | 7 | |
| cr | 45 | | 69 | | 135 | | 51 | |
| cu | 8 | | 5 | | 9 | | 2 | |
| ga | 9 | | 9 | | 11 | | 7 | |
| la | 13 | | 23 | | 19 | | 23 | |
| ni | 17 | | 19 | | 42 | | 17 | |
| pb | 5 | | 5 | | 7 | | 7 | |
| rb | 43 | | 43 | | 44 | | 44 | |
| sr | 50 | | 59 | | 75 | | 97 | |
| th | 8 | | 6 | | 8 | | 10 | |
| u | 3 | | 3 | | 3 | | 3 | |
| y | 18 | | 22 | | 16 | | 22 | |
| zn | 48 | | 50 | | 76 | | 42 | |
| zr | 190 | | 316 | | 186 | | 216 | |
| rb | 13 | | 16 | | 18 | | 10 | |

| <i>Sample</i> | 37s2 | 37s2* | 38s2 | 38 s 2 * | 39s2 | 39s2* | 40s2 | 40s2* |
|--------------------------------|--------|-------|--------|----------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.58 | 80.65 | 81.79 | 81.70 | 75.99 | 76.86 | 83.01 | 83.84 |
| TiO ₂ | 0.52 | 0.52 | 0.66 | 0.66 | 0.71 | 0.72 | 0.71 | 0.72 |
| Al ₂ O ₃ | 7.67 | 7.68 | 8.83 | 8.82 | 10.37 | 10.49 | 7.74 | 7.82 |
| Fe ₂ O ₃ | 0.99 | 0.99 | 1.04 | 1.04 | 1.11 | 1.12 | 0.69 | 0.70 |
| FeO | 2.55 | 2.55 | 1.87 | 1.87 | 2.91 | 2.94 | 1.80 | 1.82 |
| MnO | 0.07 | 0.07 | 0.04 | 0.04 | 0.03 | 0.03 | 0.04 | 0.04 |
| MgO | 2.16 | 2.16 | 1.04 | 1.04 | 1.62 | 1.64 | 1.02 | 1.03 |
| CaO | 0.30 | 0.02 | 0.79 | 0.15 | 0.55 | 0.31 | 1.17 | 0.00 |
| Na ₂ O | 2.12 | 2.12 | 1.16 | 1.16 | 1.66 | 1.68 | 1.05 | 1.06 |
| K ₂ O | 1.06 | 1.06 | 1.39 | 1.39 | 1.45 | 1.47 | 0.96 | 0.97 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.10 | 0.10 | 0.15 | 0.15 | 0.14 | 0.14 |
| H ₂ O | 2.05 | 2.05 | 2.03 | 2.03 | 2.56 | 2.59 | 1.61 | 1.63 |
| CO ₂ | 0.22 | 0.00 | 0.50 | 0.00 | 0.19 | 0.00 | 1.17 | 0.25 |
| Total | 100.41 | | 101.24 | | 99.30 | | 101.11 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 272 | | 289 | | 309 | | 161 | |
| ce | 17 | | 38 | | 71 | | 57 | |
| co | 10 | | 7 | | 10 | | 6 | |
| cr | 372 | | 172 | | 56 | | 50 | |
| cu | 11 | | 5 | | 2 | | 2 | |
| ga | 8 | | 8 | | 11 | | 6 | |
| la | 7 | | 15 | | 31 | | 21 | |
| ni | 40 | | 31 | | 30 | | 14 | |
| pb | 5 | | 8 | | 7 | | 4 | |
| rb | 29 | | 48 | | 52 | | 30 | |
| sr | 44 | | 43 | | 54 | | 40 | |
| th | 4 | | 7 | | 7 | | 5 | |
| u | 2 | | 2 | | 3 | | 3 | |
| y | 14 | | 19 | | 28 | | 22 | |
| zn | 52 | | 890 | | 68 | | 40 | |
| zr | 117 | | 228 | | 205 | | 335 | |
| rb | 5 | | 11 | | 13 | | 16 | |

| <i>Sample</i> | 1h1 | 1h1* | 2h1 | 2h1* | 3h1 | 3h1* | 4h1 | 4h1* |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 72.54 | 73.42 | 59.96 | 76.36 | 73.92 | 74.85 | 72.92 | 74.17 |
| TiO ₂ | 0.87 | 0.88 | 0.56 | 0.71 | 0.68 | 0.69 | 0.87 | 0.88 |
| Al ₂ O ₃ | 10.88 | 11.01 | 8.38 | 10.67 | 10.39 | 10.52 | 10.88 | 11.07 |
| Fe ₂ O ₃ | 2.31 | 2.34 | 0.93 | 1.18 | 1.80 | 1.82 | 2.15 | 2.19 |
| FeO | 2.93 | 2.97 | 1.32 | 1.68 | 3.29 | 3.33 | 2.64 | 2.69 |
| MnO | 0.06 | 0.06 | 0.15 | 0.19 | 0.08 | 0.08 | 0.05 | 0.05 |
| MgO | 2.26 | 2.29 | 1.70 | 2.16 | 2.27 | 2.30 | 2.26 | 2.30 |
| CaO | 0.22 | 0.00 | 12.07 | 0.48 | 0.48 | 0.09 | 0.22 | 0.22 |
| Na ₂ O | 2.00 | 2.02 | 1.34 | 1.71 | 2.26 | 2.29 | 2.00 | 2.03 |
| K ₂ O | 1.34 | 1.36 | 1.31 | 1.67 | 1.20 | 1.22 | 1.34 | 1.36 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.13 | 0.17 | 0.14 | 0.14 | 0.13 | 0.13 |
| H ₂ O+ | 3.37 | 3.41 | 2.35 | 2.99 | 2.62 | 2.65 | 2.83 | 2.88 |
| CO ₂ | 0.55 | 0.12 | 9.21 | 0.00 | 0.31 | 0.00 | 0.00 | 0.00 |
| Total | 99.46 | | 99.43 | | 99.46 | | 98.32 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 374 | | 219 | | 289 | | 331 | |
| Ce | 22 | | 36 | | 26 | | 40 | |
| Co | 15 | | 5 | | 15 | | 17 | |
| Cr | 93 | | 123 | | 87 | | 119 | |
| Cu | 23 | | 12 | | 26 | | 15 | |
| Ga | 14 | | 10 | | 12 | | 13 | |
| La | 12 | | 12 | | 9 | | 15 | |
| Ni | 50 | | 25 | | 49 | | 56 | |
| Pb | 9 | | 8 | | 6 | | 8 | |
| Rb | 57 | | 45 | | 39 | | 46 | |
| Sr | 60 | | 114 | | 77 | | 89 | |
| Th | 8 | | 7 | | 6 | | 5 | |
| U | 3 | | 1 | | 2 | | 2 | |
| Y | 21 | | 25 | | 20 | | 24 | |
| Zn | 64 | | 41 | | 64 | | 70 | |
| Zr | 212 | | 251 | | 163 | | 263 | |
| Nb | 15 | | 9 | | 6 | | 18 | |

| <i>Sample</i> | 5h1 | 5h1* | 6h1 | 6h1* | 7h1 | 7h1* | 8h1 | 8h1* |
|--------------------------------|--------|-------|--------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 75.69 | 74.99 | 75.90 | 75.83 | 75.69 | 76.98 | 72.82 | 73.42 |
| TiO ₂ | 0.83 | 0.82 | 1.00 | 1.00 | 0.66 | 0.67 | 0.87 | 0.88 |
| Al ₂ O ₃ | 10.48 | 10.38 | 9.91 | 9.90 | 8.68 | 8.83 | 10.48 | 10.57 |
| Fe ₂ O ₃ | 2.59 | 2.57 | 2.15 | 2.15 | 3.69 | 3.75 | 2.87 | 2.89 |
| FeO | 2.51 | 2.49 | 2.78 | 2.78 | 1.86 | 1.89 | 2.88 | 2.90 |
| MnO | 0.05 | 0.05 | 0.06 | 0.06 | 0.08 | 0.08 | 0.07 | 0.07 |
| MgO | 2.23 | 2.21 | 2.08 | 2.08 | 2.05 | 2.08 | 2.52 | 2.54 |
| CaO | 0.15 | 0.15 | 0.63 | 0.06 | 0.87 | 0.21 | 0.51 | 0.13 |
| Na ₂ O | 2.00 | 1.98 | 1.77 | 1.77 | 2.11 | 2.15 | 1.89 | 1.91 |
| K ₂ O | 1.48 | 1.47 | 1.21 | 1.21 | 0.80 | 0.81 | 1.43 | 1.44 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.15 | 0.15 | 0.09 | 0.09 | 0.13 | 0.13 |
| H ₂ O+ | 2.77 | 2.74 | 3.00 | 3.00 | 2.39 | 2.43 | 3.06 | 3.09 |
| CO ₂ | 0.00 | 0.00 | 0.45 | 0.00 | 0.52 | 0.00 | 0.30 | 0.00 |
| Total | 100.93 | | 101.11 | | 99.51 | | 99.86 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 319 | | 275 | | 208 | | 391 | |
| ce | 29 | | 63 | | 32 | | 37 | |
| co | 14 | | 14 | | 12 | | 19 | |
| cr | 82 | | 88 | | 106 | | 139 | |
| cu | 15 | | 16 | | 15 | | 24 | |
| ga | 13 | | 12 | | 10 | | 13 | |
| la | 13 | | 30 | | 16 | | 17 | |
| ni | 44 | | 40 | | 37 | | 57 | |
| pb | 9 | | 8 | | 9 | | 11 | |
| rb | 49 | | 43 | | 27 | | 45 | |
| sr | 76 | | 66 | | 90 | | 94 | |
| th | 5 | | 6 | | 5 | | 5 | |
| u | 3 | | 2 | | 3 | | 2 | |
| y | 21 | | 42 | | 19 | | 35 | |
| zn | 64 | | 59 | | 52 | | 70 | |
| zr | 237 | | 312 | | 153 | | 276 | |
| rb | 18 | | 12 | | 10 | | 13 | |

| <i>Sample</i> | 9h1 | 9h1* | 10h1 | 10h1* | 11h1 | 11h1* | 12h1 | 12h1* |
|--------------------------------|-------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 56.37 | 73.10 | 74.86 | 75.30 | 78.58 | 79.17 | 72.83 | 76.96 |
| TiO ₂ | 0.52 | 0.67 | 0.95 | 0.96 | 0.63 | 0.63 | 0.56 | 0.59 |
| Al ₂ O ₃ | 8.94 | 11.59 | 9.60 | 9.66 | 8.55 | 8.61 | 9.04 | 9.55 |
| Fe ₂ O ₃ | 1.82 | 2.36 | 2.46 | 2.47 | 2.21 | 2.23 | 1.92 | 2.03 |
| FeO | 1.29 | 1.67 | 2.93 | 2.95 | 1.74 | 1.75 | 1.71 | 1.81 |
| MnO | 0.17 | 0.22 | 0.07 | 0.07 | 0.08 | 0.08 | 0.05 | 0.05 |
| MgO | 1.56 | 2.02 | 2.48 | 2.49 | 1.91 | 1.92 | 1.91 | 2.02 |
| CaO | 13.47 | 0.90 | 0.62 | 0.15 | 0.54 | 0.00 | 3.23 | 0.13 |
| Na ₂ O | 0.89 | 1.15 | 1.90 | 1.91 | 1.93 | 1.94 | 2.39 | 2.53 |
| K ₂ O | 2.13 | 2.76 | 1.08 | 1.09 | 0.68 | 0.69 | 1.26 | 1.33 |
| P ₂ O ₅ | 0.10 | 0.13 | 0.14 | 0.14 | 0.09 | 0.09 | 0.09 | 0.10 |
| H ₂ O+ | 2.62 | 3.40 | 2.77 | 2.79 | 2.75 | 2.77 | 2.74 | 2.90 |
| CO ₂ | 10.06 | 0.00 | 0.37 | 0.00 | 0.47 | 0.10 | 2.45 | 0.00 |
| Total | 99.95 | | 100.26 | | 100.17 | | 100.19 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 345 | | 300 | | 194 | | 261 | |
| ce | 37 | | 42 | | 54 | | 49 | |
| co | 11 | | 15 | | 8 | | 11 | |
| cr | 92 | | 122 | | 96 | | 101 | |
| cu | 14 | | 23 | | 27 | | 22 | |
| ga | 12 | | 12 | | 10 | | 12 | |
| la | 19 | | 18 | | 25 | | 19 | |
| ni | 23 | | 41 | | 37 | | 28 | |
| pb | 6 | | 7 | | 13 | | 6 | |
| rb | 74 | | 35 | | 21 | | 45 | |
| sr | 99 | | 76 | | 80 | | 144 | |
| th | 6 | | 7 | | 4 | | 9 | |
| u | 2 | | 2 | | 3 | | 2 | |
| y | 23 | | 21 | | 19 | | 23 | |
| zn | 40 | | 65 | | 48 | | 48 | |
| zr | 210 | | 302 | | 155 | | 237 | |
| rb | 8 | | 14 | | 6 | | 10 | |

| <i>Sample</i> | 13h1 | 13h1* | 14h1 | 14h1* | 15h1 | 15h1* | 16h1 | 16h1* |
|--------------------------------|-------|-------|--------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 74.60 | 75.48 | 78.28 | 79.50 | 75.04 | 75.08 | 70.11 | 71.62 |
| TiO ₂ | 0.56 | 0.57 | 0.68 | 0.69 | 0.93 | 0.93 | 0.88 | 0.90 |
| Al ₂ O ₃ | 10.34 | 10.46 | 8.01 | 8.13 | 10.06 | 10.07 | 12.22 | 12.48 |
| Fe ₂ O ₃ | 2.33 | 2.36 | 2.17 | 2.20 | 2.36 | 2.36 | 2.57 | 2.63 |
| FeO | 1.94 | 1.96 | 1.39 | 1.41 | 2.57 | 2.57 | 2.93 | 2.99 |
| MnO | 0.07 | 0.07 | 0.09 | 0.09 | 0.06 | 0.06 | 0.06 | 0.06 |
| MgO | 2.35 | 2.38 | 2.24 | 2.27 | 2.69 | 2.69 | 2.40 | 2.45 |
| CaO | 0.68 | 0.19 | 1.24 | 0.06 | 0.30 | 0.30 | 0.31 | 0.24 |
| Na ₂ O | 2.68 | 2.71 | 1.43 | 1.45 | 1.50 | 1.50 | 2.01 | 2.05 |
| K ₂ O | 0.74 | 0.75 | 1.35 | 1.37 | 1.14 | 1.14 | 1.49 | 1.52 |
| P ₂ O ₅ | 0.08 | 0.08 | 0.10 | 0.10 | 0.14 | 0.14 | 0.14 | 0.14 |
| H ₂ O+ | 2.95 | 2.98 | 2.64 | 2.68 | 3.13 | 3.13 | 2.82 | 2.88 |
| CO ₂ | 0.39 | 0.00 | 0.93 | 0.00 | 0.00 | 0.10 | 0.06 | 0.00 |
| Total | 99.72 | | 100.58 | | 99.95 | | 98.03 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 268 | | 258 | | 287 | | 383 | |
| ce | 34 | | 51 | | 41 | | 60 | |
| co | 12 | | 14 | | 15 | | 17 | |
| cr | 76 | | 216 | | 115 | | 112 | |
| cu | 39 | | 20 | | 13 | | 14 | |
| ga | 12 | | 10 | | 12 | | 15 | |
| la | 19 | | 30 | | 18 | | 24 | |
| ni | 33 | | 35 | | 56 | | 54 | |
| pb | 7 | | 6 | | 8 | | 10 | |
| rb | 19 | | 41 | | 39 | | 52 | |
| sr | 136 | | 47 | | 60 | | 93 | |
| th | 2 | | 8 | | 6 | | 7 | |
| u | 1 | | 2 | | 3 | | 2 | |
| Y | 31 | | 39 | | 27 | | 34 | |
| zn | 47 | | 54 | | 65 | | 73 | |
| zr | 104 | | 393 | | 300 | | 254 | |
| nb | 3 | | 12 | | 13 | | 14 | |

| <i>Sample</i> | 17h1 | 17h1* | 18h1 | 18h1* | 19h1 | 19h1* | 20h1 | 20h1* |
|--------------------------------|-------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 68.25 | 69.37 | 77.85 | 82.79 | 53.44 | 72.77 | 60.53 | 74.31 |
| TiO ₂ | 0.89 | 0.90 | 0.57 | 0.61 | 0.63 | 0.86 | 0.73 | 0.90 |
| Al ₂ O ₃ | 12.86 | 13.07 | 7.38 | 7.84 | 8.70 | 11.85 | 8.09 | 9.93 |
| Fe ₂ O ₃ | 3.28 | 3.33 | 0.99 | 1.05 | 1.16 | 1.58 | 1.91 | 2.34 |
| FeO | 2.78 | 2.83 | 1.61 | 1.71 | 2.35 | 3.20 | 2.19 | 2.69 |
| MnO | 0.08 | 0.08 | 0.08 | 0.09 | 0.19 | 0.26 | 0.14 | 0.17 |
| MgO | 2.46 | 2.50 | 1.09 | 1.16 | 1.60 | 2.18 | 1.68 | 2.06 |
| CaO | 0.77 | 0.16 | 3.69 | 0.14 | 15.14 | 0.37 | 11.19 | 0.39 |
| Na ₂ O | 2.48 | 2.52 | 1.35 | 1.43 | 1.94 | 2.64 | 2.01 | 2.47 |
| K ₂ O | 1.57 | 1.60 | 1.13 | 1.20 | 1.10 | 1.50 | 1.11 | 1.36 |
| P ₂ O ₅ | 0.14 | 0.14 | 0.09 | 0.10 | 0.16 | 0.22 | 0.15 | 0.18 |
| H ₂ O+ | 3.41 | 3.47 | 1.82 | 1.93 | 1.89 | 2.57 | 2.59 | 3.18 |
| CO ₂ | 0.48 | 0.00 | 2.80 | 0.00 | 11.71 | 0.10 | 8.56 | 0.00 |
| Total | 99.48 | | 100.46 | | 100.02 | | 100.89 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 402 | | 254 | | 289 | | 283 | |
| ce | 41 | | 41 | | 57 | | 64 | |
| co | 21 | | 3 | | 7 | | 12 | |
| cr | 165 | | 76 | | 83 | | 77 | |
| cu | 19 | | 18 | | 20 | | 14 | |
| ga | 14 | | 10 | | 10 | | 10 | |
| la | 24 | | 17 | | 28 | | 36 | |
| ni | 59 | | 18 | | 33 | | 32 | |
| pb | 10 | | 7 | | 5 | | 11 | |
| rb | 53 | | 37 | | 35 | | 34 | |
| sr | 127 | | 117 | | 146 | | 105 | |
| th | 8 | | 7 | | 5 | | 5 | |
| u | 4 | | 2 | | 2 | | 3 | |
| y | 33 | | 19 | | 25 | | 28 | |
| zn | 73 | | 37 | | 46 | | 48 | |
| zr | 239 | | 203 | | 174 | | 208 | |
| nb | 17 | | 13 | | 8 | | 9 | |

Sample 21h1 21h1* 22h1 22h1* 1h3 1h3* 2h3 2h3*

chemical analyses (%)

| | | | | | | | | |
|--------------------------------|--------|-------|--------|-------|-------|-------|-------|-------|
| SiO ₂ | 68.47 | 72.92 | 80.50 | 80.80 | 70.28 | 70.63 | 72.97 | 73.10 |
| TiO ₂ | 0.62 | 0.66 | 0.76 | 0.76 | 1.10 | 1.11 | 0.92 | 0.92 |
| Al ₂ O ₃ | 10.50 | 11.18 | 8.25 | 8.28 | 12.10 | 12.16 | 10.52 | 10.54 |
| Fe ₂ O ₃ | 2.50 | 2.66 | 1.43 | 1.44 | 2.95 | 2.96 | 2.75 | 2.75 |
| FeO | 1.97 | 2.10 | 2.11 | 2.12 | 3.18 | 3.20 | 3.21 | 3.22 |
| MnO | 0.12 | 0.13 | 0.05 | 0.05 | 0.07 | 0.07 | 0.07 | 0.07 |
| MgO | 2.63 | 2.80 | 1.25 | 1.25 | 2.82 | 2.83 | 2.79 | 2.79 |
| CaO | 4.16 | 0.40 | 0.54 | 0.15 | 0.15 | 0.15 | 0.15 | 0.11 |
| Na ₂ O | 2.76 | 2.94 | 1.69 | 1.70 | 1.68 | 1.70 | 1.80 | 1.80 |
| K ₂ O | 1.17 | 1.25 | 1.13 | 1.13 | 1.55 | 1.56 | 1.13 | 1.13 |
| P ₂ O ₅ | 0.20 | 0.21 | 0.11 | 0.11 | 0.16 | 0.16 | 0.13 | 0.13 |
| H ₂ O+ | 2.55 | 2.72 | 2.19 | 2.20 | 3.43 | 3.45 | 3.42 | 3.43 |
| CO ₂ | 2.98 | 0.00 | 0.31 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 |
| Total | 100.66 | | 100.33 | | 99.51 | | 99.89 | |

trace elements (p.p.m)

| | | | | |
|----|-----|-----|-----|-----|
| ba | 281 | 298 | 328 | 256 |
| ce | 58 | 25 | 67 | 52 |
| co | 12 | 9 | 21 | 12 |
| cr | 140 | 74 | 150 | 154 |
| cu | 14 | 8 | 15 | 21 |
| ga | 13 | 10 | 16 | 14 |
| la | 31 | 12 | 30 | 22 |
| ni | 53 | 20 | 66 | 56 |
| pb | 7 | 5 | 11 | 11 |
| rb | 35 | 37 | 53 | 38 |
| sr | 190 | 67 | 71 | 63 |
| th | 7 | 4 | 8 | 7 |
| u | 3 | 2 | 2 | 3 |
| y | 39 | 15 | 25 | 20 |
| zn | 62 | 45 | 83 | 76 |
| zr | 266 | 270 | 368 | 242 |
| rb | 10 | 11 | 19 | 10 |

| <i>Sample</i> | 3h3 | 3h3* | 4h3 | 4h3* | 5h3 | 5h3* | 6h3 | 6h3* |
|--------------------------------|--------|-------|-------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 78.61 | 78.82 | 74.48 | 76.56 | 76.83 | 77.37 | 59.72 | 74.85 |
| TiO ₂ | 0.75 | 0.75 | 0.63 | 0.65 | 0.75 | 0.76 | 0.44 | 0.55 |
| Al ₂ O ₃ | 9.93 | 9.96 | 9.60 | 9.87 | 9.18 | 9.24 | 8.93 | 11.19 |
| Fe ₂ O ₃ | 1.32 | 1.32 | 3.35 | 3.44 | 2.50 | 2.52 | 1.45 | 1.82 |
| FeO | 2.04 | 2.05 | 1.51 | 1.55 | 2.29 | 2.31 | 1.34 | 1.68 |
| MnO | 0.04 | 0.04 | 0.06 | 0.06 | 0.05 | 0.05 | 0.07 | 0.09 |
| MgO | 1.54 | 1.54 | 1.92 | 1.97 | 1.92 | 1.93 | 1.98 | 2.48 |
| CaO | 0.11 | 0.00 | 1.62 | 0.37 | 0.29 | 0.10 | 11.48 | 1.89 |
| Na ₂ O | 1.63 | 1.63 | 1.07 | 1.10 | 1.49 | 1.50 | 0.56 | 0.70 |
| K ₂ O | 1.50 | 1.50 | 1.71 | 1.76 | 1.18 | 1.19 | 1.54 | 1.99 |
| P ₂ O ₅ | 0.14 | 0.14 | 0.11 | 0.11 | 0.12 | 0.12 | 0.09 | 0.11 |
| H ₂ O+ | 2.13 | 2.14 | 2.46 | 2.53 | 2.88 | 2.90 | 2.14 | 2.68 |
| CO ₂ | 0.47 | 0.10 | 0.99 | 0.00 | 0.15 | 0.00 | 7.85 | 0.00 |
| Total | 100.22 | | 99.53 | | 99.64 | | 97.61 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 277 | | 324 | | 267 | | 333 | |
| ce | 18 | | 53 | | 66 | | 37 | |
| co | 6 | | 13 | | 12 | | 8 | |
| cr | 57 | | 115 | | 90 | | 68 | |
| cu | 12 | | 15 | | 12 | | 12 | |
| ga | 11 | | 13 | | 10 | | 12 | |
| la | 6 | | 31 | | 30 | | 18 | |
| ni | 29 | | 36 | | 39 | | 41 | |
| pb | 6 | | 8 | | 9 | | 4 | |
| rb | 49 | | 60 | | 39 | | 49 | |
| sr | 49 | | 65 | | 56 | | 115 | |
| th | 6 | | 9 | | 6 | | 5 | |
| u | 3 | | 3 | | 2 | | 3 | |
| y | 15 | | 32 | | 20 | | 22 | |
| zn | 47 | | 50 | | 57 | | 45 | |
| zr | 263 | | 253 | | 250 | | 139 | |
| rb | 17 | | 11 | | 9 | | 7 | |

| <i>Sample</i> | 7h3 | 7h3* | 8h3 | 8h3* | 9h3 | 9h3* | 10h3 | 10h3* |
|--------------------------------|-------|-------|-------|-------|--------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.43 | 83.01 | 71.14 | 71.89 | 78.56 | 79.04 | 76.43 | 79.83 |
| TiO ₂ | 0.54 | 0.56 | 0.75 | 0.76 | 0.95 | 0.96 | 0.69 | 0.72 |
| Al ₂ O ₃ | 7.41 | 7.65 | 11.60 | 11.72 | 7.86 | 7.91 | 9.02 | 9.42 |
| Fe ₂ O ₃ | 1.01 | 1.04 | 2.86 | 2.89 | 2.92 | 2.94 | 1.39 | 1.45 |
| FeO | 1.53 | 1.58 | 2.57 | 2.60 | 2.00 | 2.01 | 1.40 | 1.46 |
| MnO | 0.08 | 0.08 | 0.08 | 0.08 | 0.09 | 0.09 | 0.05 | 0.05 |
| MgO | 1.20 | 1.24 | 2.88 | 2.91 | 2.14 | 2.15 | 1.41 | 1.47 |
| CaO | 1.53 | 0.05 | 0.70 | 0.19 | 0.38 | 0.01 | 1.55 | 0.00 |
| Na ₂ O | 1.65 | 1.70 | 3.13 | 3.16 | 1.17 | 1.18 | 0.88 | 0.92 |
| K ₂ O | 1.12 | 1.16 | 0.67 | 0.68 | 0.82 | 0.83 | 1.73 | 1.81 |
| P ₂ O ₅ | 0.10 | 0.10 | 0.08 | 0.08 | 0.11 | 0.11 | 0.14 | 0.15 |
| H ₂ O+ | 1.77 | 1.83 | 3.00 | 3.03 | 2.73 | 2.75 | 2.33 | 2.43 |
| CO ₂ | 1.17 | 0.00 | 0.40 | 0.00 | 0.29 | 0.00 | 1.25 | 0.27 |
| Total | 99.55 | | 99.87 | | 100.05 | | 98.28 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 532 | | 265 | | 225 | | 322 | |
| ce | 33 | | 28 | | 37 | | 24 | |
| co | 8 | | 20 | | 15 | | 7 | |
| cr | 46 | | 94 | | 113 | | 60 | |
| cu | 19 | | 27 | | 13 | | 13 | |
| ga | 11 | | 11 | | 10 | | 11 | |
| la | 13 | | 15 | | 17 | | 11 | |
| ni | 28 | | 36 | | 42 | | 24 | |
| pb | 7 | | 7 | | 10 | | 7 | |
| rb | 37 | | 18 | | 26 | | 54 | |
| sr | 91 | | 181 | | 50 | | 71 | |
| th | 6 | | 1 | | 5 | | 7 | |
| u | 2 | | 2 | | 2 | | 1 | |
| y | 15 | | 18 | | 18 | | 20 | |
| zn | 39 | | 59 | | 58 | | 41 | |
| zr | 178 | | 115 | | 235 | | 262 | |
| rb | 14 | | 6 | | 12 | | 12 | |

| <i>Sample</i> | 11h3 | 11h3* | 12h3 | 12h3* | 13h3 | 13h3* | 14h3 | 14h3* |
|--------------------------------|-------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 63.10 | 72.92 | 69.37 | 79.23 | 78.28 | 78.70 | 74.50 | 75.38 |
| TiO ₂ | 0.72 | 0.83 | 0.47 | 0.54 | 0.70 | 0.70 | 0.86 | 0.87 |
| Al ₂ O ₃ | 10.38 | 12.00 | 7.32 | 8.36 | 8.88 | 8.93 | 9.75 | 9.87 |
| Fe ₂ O ₃ | 1.70 | 1.96 | 1.82 | 2.08 | 2.22 | 2.23 | 3.48 | 3.52 |
| FeO | 2.01 | 2.32 | 1.69 | 1.93 | 1.68 | 1.69 | 1.84 | 1.86 |
| MnO | 0.17 | 0.20 | 0.13 | 0.15 | 0.05 | 0.05 | 0.06 | 0.06 |
| MgO | 1.96 | 2.27 | 1.75 | 2.00 | 1.87 | 1.88 | 2.38 | 2.41 |
| CaO | 7.80 | 0.60 | 7.36 | 0.41 | 0.62 | 0.28 | 0.86 | 0.07 |
| Na ₂ O | 1.01 | 1.17 | 0.89 | 1.02 | 1.27 | 1.28 | 1.06 | 1.07 |
| K ₂ O | 1.78 | 2.06 | 1.04 | 1.19 | 1.22 | 1.23 | 1.29 | 1.31 |
| P ₂ O ₅ | 0.14 | 0.16 | 0.14 | 0.16 | 0.10 | 0.10 | 0.13 | 0.13 |
| H ₂ O+ | 3.01 | 3.48 | 2.54 | 2.90 | 2.89 | 2.91 | 3.38 | 3.42 |
| CO ₂ | 5.73 | 0.00 | 5.51 | 0.00 | 0.27 | 0.00 | 0.62 | 0.00 |
| Total | 99.54 | | 100.06 | | 100.08 | | 100.24 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 358 | | 212 | | 284 | | 300 | |
| ce | 39 | | 39 | | 35 | | 34 | |
| co | 9 | | 11 | | 10 | | 16 | |
| cr | 132 | | 144 | | 113 | | 126 | |
| cu | 15 | | 19 | | 15 | | 14 | |
| ga | 12 | | 10 | | 11 | | 12 | |
| la | 13 | | 17 | | 10 | | 13 | |
| ni | 48 | | 51 | | 44 | | 57 | |
| pb | 9 | | 7 | | 9 | | 8 | |
| rb | 58 | | 34 | | 38 | | 44 | |
| sr | 125 | | 211 | | 60 | | 47 | |
| th | 8 | | 6 | | 5 | | 6 | |
| u | 3 | | 2 | | 3 | | 3 | |
| y | 23 | | 22 | | 14 | | 15 | |
| zn | 52 | | 46 | | 47 | | 58 | |
| zr | 214 | | 130 | | 228 | | 260 | |
| rb | 10 | | 9 | | 10 | | 14 | |

| <i>Sample</i> | 15h3 | 15h3* | 16h3 | 16h3* | 17h3 | 17h3* | 18h3 | 18h3* |
|--------------------------------|-------|-------|-------|-------|--------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 65.58 | 75.82 | 64.84 | 72.42 | 78.22 | 78.72 | 69.29 | 75.77 |
| TiO ₂ | 0.85 | 0.98 | 0.74 | 0.83 | 0.88 | 0.89 | 0.99 | 1.08 |
| Al ₂ O ₃ | 8.62 | 9.97 | 9.89 | 11.05 | 8.75 | 8.81 | 9.15 | 10.01 |
| Fe ₂ O ₃ | 1.69 | 1.95 | 2.08 | 2.32 | 1.57 | 1.58 | 1.82 | 1.99 |
| FeO | 2.23 | 2.58 | 2.56 | 2.86 | 2.38 | 2.40 | 2.54 | 2.78 |
| MnO | 0.17 | 0.20 | 0.12 | 0.13 | 0.05 | 0.05 | 0.09 | 0.10 |
| MgO | 1.73 | 2.00 | 2.03 | 2.27 | 1.82 | 1.83 | 1.68 | 1.84 |
| CaO | 7.68 | 0.27 | 6.31 | 0.00 | 0.77 | 0.11 | 4.80 | 0.43 |
| Na ₂ O | 1.28 | 1.48 | 2.09 | 2.33 | 1.61 | 1.62 | 1.94 | 2.12 |
| K ₂ O | 1.24 | 1.43 | 1.16 | 1.30 | 1.03 | 1.04 | 1.25 | 1.37 |
| P ₂ O ₅ | 0.13 | 0.15 | 0.19 | 0.21 | 0.13 | 0.13 | 0.10 | 0.11 |
| H ₂ O+ | 2.71 | 3.13 | 2.75 | 3.07 | 2.80 | 2.82 | 2.15 | 2.35 |
| CO ₂ | 5.86 | 0.00 | 5.04 | 1.18 | 0.52 | 0.00 | 3.47 | 0.00 |
| Total | 99.80 | | 99.83 | | 100.54 | | 99.32 | |
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 290 | | 293 | | 221 | | 302 | |
| ce | 45 | | 40 | | 34 | | 37 | |
| co | 10 | | 13 | | 12 | | 13 | |
| cr | 160 | | 145 | | 87 | | 297 | |
| cu | 17 | | 23 | | 13 | | 22 | |
| ga | 12 | | 11 | | 11 | | 13 | |
| la | 20 | | 18 | | 13 | | 19 | |
| ni | 41 | | 50 | | 38 | | 45 | |
| pb | 8 | | 7 | | 8 | | 7 | |
| rb | 40 | | 40 | | 35 | | 41 | |
| sr | 97 | | 125 | | 62 | | 136 | |
| th | 6 | | 6 | | 3 | | 6 | |
| u | 3 | | 2 | | 3 | | 2 | |
| y | 23 | | 26 | | 12 | | 27 | |
| zn | 50 | | 62 | | 53 | | 62 | |
| zr | 279 | | 222 | | 263 | | 326 | |
| rb | 11 | | 9 | | 16 | | 16 | |

| <i>Sample</i> | 19h3 | 19h3* | 1h4 | 1h4* | 2h4 | 2h4* | 3h4 | 3h4* |
|--------------------------------|--------|-------|--------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 79.36 | 80.62 | 64.46 | 80.12 | 81.37 | 83.51 | 73.54 | 78.73 |
| TiO ₂ | 0.72 | 0.73 | 0.51 | 0.63 | 0.49 | 0.50 | 0.61 | 0.65 |
| Al ₂ O ₃ | 8.38 | 8.51 | 6.55 | 8.14 | 7.00 | 7.18 | 7.66 | 8.20 |
| Fe ₂ O ₃ | 1.66 | 1.69 | 0.99 | 1.23 | 0.78 | 0.80 | 2.44 | 2.61 |
| FeO | 2.11 | 2.14 | 1.50 | 1.86 | 1.69 | 1.73 | 1.41 | 1.51 |
| MnO | 0.05 | 0.05 | 0.22 | 0.27 | 0.05 | 0.05 | 0.08 | 0.09 |
| MgO | 1.18 | 1.20 | 1.31 | 1.63 | 1.27 | 1.30 | 2.06 | 2.21 |
| CaO | 1.04 | 0.05 | 11.90 | 0.63 | 0.47 | 0.17 | 3.91 | 0.49 |
| Na ₂ O | 1.60 | 1.63 | 1.74 | 2.16 | 1.01 | 1.04 | 0.65 | 0.70 |
| K ₂ O | 1.15 | 1.17 | 0.99 | 1.23 | 1.25 | 1.28 | 1.41 | 1.51 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.10 | 0.12 | 0.09 | 0.09 | 0.10 | 0.11 |
| H ₂ O+ | 2.05 | 2.08 | 1.57 | 1.95 | 2.28 | 2.34 | 2.99 | 3.20 |
| CO ₂ | 0.78 | 0.00 | 8.97 | 1.18 | 1.03 | 0.00 | 2.72 | 0.00 |
| Total | 100.21 | | 100.82 | | 99.78 | | 99.58 | |

| | | | | | | | | |
|-------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m)</i> | | | | | | | | |
| ba | 280 | | 235 | | 232 | | 239 | |
| ce | 49 | | 48 | | 51 | | 53 | |
| co | 6 | | 7 | | 7 | | 8 | |
| cr | 63 | | 48 | | 31 | | 162 | |
| cu | 14 | | 15 | | 13 | | 13 | |
| ga | 10 | | 8 | | 8 | | 10 | |
| la | 19 | | 21 | | 19 | | 26 | |
| ni | 22 | | 22 | | 17 | | 32 | |
| pb | 7 | | 7 | | 4 | | 6 | |
| rb | 39 | | 32 | | 39 | | 49 | |
| sr | 80 | | 151 | | 75 | | 52 | |
| th | 8 | | 5 | | 4 | | 8 | |
| u | 2 | | 2 | | 2 | | 4 | |
| y | 19 | | 20 | | 17 | | 25 | |
| zn | 42 | | 33 | | 37 | | 46 | |
| zr | 290 | | 182 | | 155 | | 333 | |
| rb | 13 | | 11 | | 13 | | 8 | |

| <i>Sample</i> | 1t1 | 1t1* | 2t1 | 2t1* | 3t1 | 3t1* | 4t1 | 4t1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.63 | 79.84 | 72.49 | 72.76 | 72.18 | 71.93 | 77.87 | 77.31 |
| TiO ₂ | 0.65 | 0.64 | 0.70 | 0.70 | 0.93 | 0.93 | 0.77 | 0.76 |
| Al ₂ O ₃ | 8.67 | 8.59 | 11.11 | 11.15 | 10.01 | 9.97 | 8.53 | 8.47 |
| Fe ₂ O ₃ | 1.48 | 1.47 | 1.95 | 1.96 | 2.66 | 2.65 | 1.40 | 1.39 |
| FeO | 1.28 | 1.27 | 1.73 | 1.74 | 2.76 | 2.75 | 2.67 | 2.65 |
| MnO | 0.08 | 0.08 | 0.06 | 0.06 | 0.05 | 0.05 | 0.08 | 0.08 |
| MgO | 1.96 | 1.94 | 2.68 | 2.69 | 4.04 | 4.03 | 2.94 | 2.92 |
| CaO | 0.88 | 0.68 | 1.94 | 1.40 | 1.41 | 1.33 | 0.72 | 0.53 |
| Na ₂ O | 2.50 | 2.48 | 3.12 | 3.13 | 2.07 | 2.06 | 2.40 | 2.38 |
| K ₂ O | 1.21 | 1.20 | 1.56 | 1.57 | 1.03 | 1.03 | 0.92 | 0.91 |
| P ₂ O ₅ | 0.08 | 0.08 | 0.28 | 0.28 | 0.15 | 0.15 | 0.12 | 0.12 |
| H ₂ O+ | 1.76 | 1.74 | 2.55 | 2.56 | 3.14 | 3.13 | 2.49 | 2.47 |
| CO ₂ | 0.15 | 0.00 | 0.43 | 0.00 | 0.06 | 0.00 | 0.15 | 0.00 |
| Total | 101.33 | | 100.59 | | 100.47 | | 101.03 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 367 | | 437 | | 588 | | 346 | |
| ce | 31 | | 36 | | 40 | | 40 | |
| co | 9 | | 9 | | 18 | | 14 | |
| cr | 87 | | 107 | | 159 | | 134 | |
| cu | 16 | | 12 | | 27 | | 29 | |
| ga | 11 | | 11 | | 13 | | 9 | |
| la | 10 | | 14 | | 13 | | 17 | |
| ni | 28 | | 35 | | 63 | | 39 | |
| pb | 14 | | 16 | | 10 | | 64 | |
| rb | 32 | | 38 | | 32 | | 29 | |
| sr | 179 | | 230 | | 230 | | 135 | |
| th | 7 | | 7 | | 8 | | 8 | |
| u | 2 | | 2 | | 3 | | 3 | |
| y | 22 | | 27 | | 27 | | 21 | |
| zn | 62 | | 90 | | 55 | | 80 | |
| zr | 184 | | 154 | | 171 | | 191 | |
| nb | 11 | | 12 | | 13 | | 10 | |

| <i>Sample</i> | 5t1 | 5t1* | 6t1 | 6t1* | 7t1 | 7t1* | 8t1 | 8t1* |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 68.35 | 68.74 | 74.31 | 74.80 | 70.68 | 71.24 | 70.88 | 71.11 |
| TiO ₂ | 0.59 | 0.59 | 0.82 | 0.83 | 0.87 | 0.88 | 0.86 | 0.86 |
| Al ₂ O ₃ | 12.93 | 13.00 | 9.75 | 9.81 | 11.62 | 11.71 | 11.52 | 11.56 |
| Fe ₂ O ₃ | 3.38 | 3.40 | 2.22 | 2.23 | 2.17 | 2.19 | 2.20 | 2.21 |
| FeO | 1.21 | 1.22 | 2.88 | 2.90 | 3.55 | 3.58 | 3.18 | 3.19 |
| MnO | 0.09 | 0.09 | 0.05 | 0.05 | 0.05 | 0.05 | 0.10 | 0.10 |
| MgO | 4.41 | 4.44 | 2.82 | 2.84 | 3.14 | 3.17 | 2.94 | 2.95 |
| CaO | 0.41 | 0.18 | 1.00 | 0.74 | 0.52 | 0.28 | 0.82 | 0.66 |
| Na ₂ O | 2.11 | 2.12 | 1.81 | 1.82 | 2.24 | 2.26 | 2.40 | 2.41 |
| K ₂ O | 3.01 | 3.03 | 1.05 | 1.06 | 1.34 | 1.35 | 1.73 | 1.74 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.13 | 0.13 | 0.14 | 0.14 | 0.13 | 0.13 |
| H ₂ O+ | 3.04 | 3.06 | 2.77 | 2.79 | 3.13 | 3.15 | 3.08 | 3.09 |
| CO ₂ | 0.18 | 0.00 | 0.21 | 0.00 | 0.19 | 0.00 | 0.13 | 0.00 |
| Total | 99.82 | | 99.79 | | 99.63 | | 99.93 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 1288 | | 266 | | 305 | | 346 | |
| ce | 42 | | 47 | | 39 | | 29 | |
| co | 14 | | 14 | | 18 | | 16 | |
| cr | 148 | | 133 | | 158 | | 229 | |
| cu | 4 | | 13 | | 17 | | 9 | |
| ga | 13 | | 11 | | 14 | | 13 | |
| la | 18 | | 14 | | 6 | | 2 | |
| ni | 50 | | 49 | | 52 | | 57 | |
| pb | 19 | | 9 | | 7 | | 6 | |
| rb | 97 | | 39 | | 52 | | 57 | |
| sr | 220 | | 172 | | 154 | | 105 | |
| th | 10 | | 9 | | 7 | | 9 | |
| u | 3 | | 2 | | 2 | | 4 | |
| y | 18 | | 23 | | 22 | | 23 | |
| zn | 116 | | 96 | | 90 | | 97 | |
| zr | 154 | | 219 | | 202 | | 199 | |
| rb | 14 | | 10 | | 14 | | 16 | |

| Sample | 9t1 | 9t1* | 10t1 | 10t1* | 11t1 | 11t1* | 12t1 | 12t1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 73.60 | 73.57 | 79.41 | 79.18 | 70.31 | 69.96 | 71.83 | 71.86 |
| TiO ₂ | 0.81 | 0.81 | 0.69 | 0.69 | 1.03 | 1.02 | 0.87 | 0.87 |
| Al ₂ O ₃ | 10.70 | 10.70 | 8.28 | 8.26 | 11.03 | 10.98 | 11.11 | 11.12 |
| Fe ₂ O ₃ | 2.03 | 2.03 | 1.18 | 1.18 | 2.04 | 2.03 | 2.24 | 2.24 |
| FeO | 2.92 | 2.92 | 2.66 | 2.65 | 4.02 | 4.00 | 3.11 | 3.11 |
| MnO | 0.07 | 0.07 | 0.07 | 0.07 | 0.12 | 0.12 | 0.09 | 0.09 |
| MgO | 3.02 | 3.02 | 2.30 | 2.29 | 3.29 | 3.27 | 3.14 | 3.14 |
| CaO | 0.78 | 0.55 | 0.54 | 0.39 | 1.53 | 1.46 | 1.20 | 1.02 |
| Na ₂ O | 1.89 | 1.89 | 2.01 | 2.00 | 3.22 | 3.20 | 2.16 | 2.16 |
| K ₂ O | 1.36 | 1.36 | 1.05 | 1.05 | 1.11 | 1.10 | 1.26 | 1.26 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.09 | 0.09 | 0.17 | 0.17 | 0.15 | 0.15 |
| H ₂ O+ | 2.97 | 2.97 | 2.16 | 2.15 | 2.69 | 2.68 | 2.97 | 2.97 |
| CO ₂ | 0.18 | 0.00 | 0.12 | 0.00 | 0.05 | 0.00 | 0.14 | 0.00 |
| Total | 100.42 | | 100.56 | | 100.60 | | 100.26 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 268 | | 353 | | 364 | | 352 | |
| ce | 37 | | 25 | | 51 | | 37 | |
| co | 15 | | 11 | | 11 | | 17 | |
| cr | 138 | | 137 | | 150 | | 146 | |
| cu | 15 | | 9 | | 17 | | 6 | |
| ga | 13 | | 9 | | 14 | | 11 | |
| la | 5 | | 5 | | 17 | | 14 | |
| ni | 43 | | 36 | | 40 | | 52 | |
| pb | 13 | | 8 | | 13 | | 22 | |
| rb | 47 | | 32 | | 33 | | 41 | |
| sr | 98 | | 104 | | 150 | | 95 | |
| th | 9 | | 6 | | 9 | | 6 | |
| u | 4 | | 3 | | 1 | | 1 | |
| y | 20 | | 17 | | 30 | | 26 | |
| zn | 86 | | 65 | | 85 | | 108 | |
| zr | 188 | | 171 | | 285 | | 203 | |
| rb | 10 | | 11 | | 16 | | 18 | |

| <i>Sample</i> | 13t1 | 13t1* | 14t1 | 14t1* | 16t1 | 16t1* | 17t1 | 17t1* |
|--------------------------------|-------|-------|-------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 78.77 | 79.67 | 72.37 | 72.87 | 74.65 | 78.51 | 77.69 | 78.09 |
| TiO ₂ | 0.68 | 0.69 | 0.89 | 0.90 | 0.74 | 0.78 | 0.61 | 0.61 |
| Al ₂ O ₃ | 8.60 | 8.70 | 11.32 | 11.40 | 8.51 | 8.95 | 9.22 | 9.27 |
| Fe ₂ O ₃ | 1.34 | 1.36 | 1.64 | 1.65 | 1.41 | 1.48 | 1.03 | 1.04 |
| FeO | 2.48 | 2.51 | 3.82 | 3.85 | 2.82 | 2.97 | 3.24 | 3.26 |
| MnO | 0.06 | 0.06 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 |
| MgO | 2.01 | 2.03 | 2.75 | 2.77 | 1.94 | 2.04 | 2.05 | 2.06 |
| CaO | 0.30 | 0.20 | 0.45 | 0.34 | 2.02 | 0.04 | 0.85 | 0.32 |
| Na ₂ O | 1.54 | 1.56 | 1.93 | 1.94 | 1.79 | 1.88 | 1.84 | 1.85 |
| K ₂ O | 1.02 | 1.03 | 1.24 | 1.25 | 0.94 | 0.99 | 1.26 | 1.27 |
| P ₂ O ₅ | 0.09 | 0.09 | 0.13 | 0.13 | 0.11 | 0.12 | 0.11 | 0.11 |
| H ₂ O+ | 2.08 | 2.10 | 2.82 | 2.84 | 2.05 | 2.16 | 2.04 | 2.05 |
| CO ₂ | 0.08 | 0.00 | 0.09 | 0.00 | 1.56 | 0.00 | 0.42 | 0.00 |
| Total | 99.03 | | 99.50 | | 98.60 | | 100.41 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 212 | | 260 | | 243 | | 300 | |
| ce | 41 | | 47 | | 42 | | 43 | |
| co | 11 | | 13 | | 15 | | 6 | |
| cr | 95 | | 123 | | 110 | | 81 | |
| cu | 20 | | 9 | | 15 | | 12 | |
| ga | 10 | | 12 | | 9 | | 10 | |
| la | 13 | | 17 | | 25 | | 24 | |
| ni | 32 | | 45 | | 39 | | 47 | |
| pb | 9 | | 8 | | 12 | | 26 | |
| rb | 33 | | 45 | | 31 | | 44 | |
| sr | 70 | | 95 | | 92 | | 87 | |
| th | 4 | | 9 | | 4 | | 9 | |
| u | 2 | | 3 | | 1 | | 4 | |
| y | 13 | | 19 | | 37 | | 21 | |
| zn | 68 | | 85 | | 61 | | 65 | |
| zr | 188 | | 216 | | 181 | | 130 | |
| rb | 14 | | 9 | | 10 | | 10 | |

| <i>Sample</i> | 1c1 | 1c1* | 2c1 | 2c1* | 3c1 | 3c1* | 4c1 | 4c1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 74.97 | 74.13 | 81.23 | 81.68 | 74.06 | 74.55 | 76.94 | 76.76 |
| TiO ₂ | 0.92 | 0.91 | 0.63 | 0.63 | 1.10 | 1.11 | 0.81 | 0.81 |
| Al ₂ O ₃ | 10.48 | 10.36 | 6.74 | 6.78 | 10.52 | 10.59 | 9.98 | 9.96 |
| Fe ₂ O ₃ | 2.39 | 2.36 | 2.62 | 2.63 | 2.27 | 2.28 | 1.73 | 1.73 |
| FeO | 3.31 | 3.27 | 1.36 | 1.37 | 2.63 | 2.65 | 3.09 | 3.08 |
| MnO | 0.06 | 0.06 | 0.06 | 0.06 | 0.05 | 0.05 | 0.05 | 0.05 |
| MgO | 2.22 | 2.20 | 2.31 | 2.32 | 2.11 | 2.12 | 1.79 | 1.79 |
| CaO | 1.03 | 0.82 | 0.50 | 0.00 | 1.07 | 0.36 | 0.93 | 0.78 |
| Na ₂ O | 1.57 | 1.55 | 1.57 | 1.58 | 2.48 | 2.50 | 1.65 | 1.65 |
| K ₂ O | 1.23 | 1.22 | 1.19 | 1.20 | 1.17 | 1.18 | 1.20 | 1.20 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.05 | 0.05 | 0.20 | 0.20 | 0.11 | 0.11 |
| H ₂ O+ | 3.05 | 3.02 | 1.61 | 1.62 | 2.40 | 2.42 | 2.11 | 2.10 |
| CO ₂ | 0.16 | 0.00 | 0.40 | 0.08 | 0.56 | 0.00 | 0.12 | 0.00 |
| Total | 101.48 | | 100.27 | | 100.62 | | 100.50 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 263 | | 188 | | 213 | | 278 | |
| ce | 63 | | 24 | | 71 | | 52 | |
| co | 15 | | 13 | | 9 | | 15 | |
| cr | 221 | | 616 | | 113 | | 98 | |
| cu | 10 | | 4 | | 10 | | 13 | |
| ga | 12 | | 8 | | 10 | | 10 | |
| la | 24 | | 11 | | 24 | | 21 | |
| ni | 31 | | 94 | | 34 | | 34 | |
| pb | 13 | | 14 | | 9 | | 10 | |
| rb | 44 | | 42 | | 46 | | 40 | |
| sr | 92 | | 57 | | 112 | | 89 | |
| th | 8 | | 6 | | 7 | | 7 | |
| u | 3 | | 3 | | 3 | | 3 | |
| y | 26 | | 18 | | 29 | | 25 | |
| zn | 75 | | 59 | | 70 | | 67 | |
| zr | 295 | | 196 | | 361 | | 241 | |
| nb | 13 | | 10 | | 18 | | 14 | |

| <i>Sample</i> | 5c1 | 5c1* | 6c1 | 6c1* | 7c1 | 7c1* |
|--------------------------------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | |
| SiO ₂ | 67.14 | 66.20 | 75.05 | 75.15 | 80.53 | 79.79 |
| TiO ₂ | 0.91 | 0.90 | 0.77 | 0.77 | 0.58 | 0.57 |
| Al ₂ O ₃ | 13.46 | 13.27 | 9.59 | 9.60 | 8.50 | 8.42 |
| Fe ₂ O ₃ | 3.55 | 3.50 | 2.56 | 2.56 | 2.19 | 2.17 |
| FeO | 2.75 | 2.71 | 2.28 | 2.28 | 2.09 | 2.07 |
| MnO | 0.07 | 0.07 | 0.07 | 0.07 | 0.04 | 0.04 |
| MgO | 3.10 | 3.06 | 2.84 | 2.84 | 1.69 | 1.67 |
| CaO | 1.60 | 1.55 | 0.55 | 0.47 | 0.96 | 0.88 |
| Na ₂ O | 4.34 | 4.28 | 2.18 | 2.18 | 1.36 | 1.35 |
| K ₂ O | 1.51 | 1.49 | 1.54 | 1.54 | 1.31 | 1.30 |
| P ₂ O ₅ | 0.14 | 0.14 | 0.12 | 0.12 | 0.09 | 0.09 |
| H ₂ O+ | 2.88 | 2.84 | 2.39 | 2.39 | 1.66 | 1.64 |
| CO ₂ | 0.02 | 0.00 | 0.06 | 0.00 | 0.06 | 0.00 |
| Total | 101.44 | | 100.00 | | 101.04 | |

| | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | |
| ba | 587 | | 278 | | 273 | |
| ce | 62 | | 39 | | 45 | |
| co | 23 | | 17 | | 10 | |
| cr | 281 | | 410 | | 132 | |
| cu | 31 | | 12 | | 9 | |
| ga | 13 | | 13 | | 9 | |
| la | 22 | | 16 | | 20 | |
| ni | 58 | | 98 | | 34 | |
| pb | 21 | | 15 | | 9 | |
| rb | 32 | | 50 | | 35 | |
| sr | 323 | | 63 | | 90 | |
| th | 9 | | 8 | | 6 | |
| u | 3 | | 2 | | 2 | |
| y | 35 | | 20 | | 18 | |
| zn | 107 | | 80 | | 68 | |
| zr | 163 | | 204 | | 135 | |
| rb | 11 | | 13 | | 6 | |

| <i>Sample</i> | 1ne1 | 1ne1* | 2ne1 | 2ne1* | 3ne1 | 3ne1* | 4ne1 | 4ne1* |
|--------------------------------|--------|-------|--------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 79.60 | 79.45 | 74.16 | 73.91 | 71.71 | 72.50 | 76.77 | 76.73 |
| TiO ₂ | 0.69 | 0.69 | 0.90 | 0.90 | 0.92 | 0.93 | 0.83 | 0.83 |
| Al ₂ O ₃ | 8.82 | 8.80 | 10.71 | 10.67 | 10.79 | 10.91 | 9.32 | 9.31 |
| Fe ₂ O ₃ | 1.76 | 1.76 | 1.76 | 1.75 | 2.03 | 2.05 | 1.38 | 1.38 |
| FeO | 2.33 | 2.33 | 3.63 | 3.62 | 3.70 | 3.74 | 2.96 | 2.96 |
| MnO | 0.05 | 0.05 | 0.08 | 0.08 | 0.09 | 0.09 | 0.05 | 0.05 |
| MgO | 1.95 | 1.95 | 2.73 | 2.72 | 3.03 | 3.06 | 2.45 | 2.45 |
| CaO | 0.69 | 0.57 | 0.83 | 0.70 | 0.97 | 0.88 | 1.03 | 0.83 |
| Na ₂ O | 1.70 | 1.70 | 2.08 | 2.07 | 1.71 | 1.73 | 2.04 | 2.04 |
| K ₂ O | 0.80 | 0.80 | 1.12 | 1.12 | 1.15 | 1.16 | 0.81 | 0.81 |
| P ₂ O ₅ | 0.09 | 0.09 | 0.12 | 0.12 | 0.11 | 0.11 | 0.11 | 0.11 |
| H ₂ O+ | 1.82 | 1.82 | 2.34 | 2.33 | 2.80 | 2.83 | 2.51 | 2.51 |
| CO ₂ | 0.09 | 0.00 | 0.10 | 0.00 | 0.08 | 0.00 | 0.16 | 0.00 |
| Total | 100.37 | | 100.54 | | 99.07 | | 100.41 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 150 | | 251 | | 272 | | 185 | |
| ce | 31 | | 46 | | 39 | | 38 | |
| co | 8 | | 15 | | 18 | | 15 | |
| cr | 82 | | 106 | | 124 | | 98 | |
| cu | 5 | | 8 | | 13 | | 8 | |
| ga | 9 | | 13 | | 12 | | 10 | |
| la | 9 | | 17 | | 19 | | 10 | |
| ni | 32 | | 50 | | 52 | | 38 | |
| pb | 15 | | 13 | | 17 | | 9 | |
| rb | 28 | | 38 | | 41 | | 27 | |
| sr | 94 | | 96 | | 101 | | 105 | |
| th | 6 | | 8 | | 6 | | 4 | |
| u | 3 | | 3 | | 3 | | 3 | |
| y | 19 | | 29 | | 32 | | 28 | |
| zn | 67 | | 82 | | 96 | | 73 | |
| zr | 157 | | 201 | | 205 | | 201 | |
| rb | 10 | | 11 | | 12 | | 11 | |

| <i>Sample</i> | 5ne1 | 5ne1* | 6ne1 | 6ne1* | 7ne1 | 7ne1* | 8ne1 | 8ne1* |
|--------------------------------|-------|-------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 76.12 | 76.74 | 80.60 | 80.23 | 80.22 | 82.11 | 75.77 | 75.87 |
| TiO ₂ | 0.81 | 0.82 | 0.66 | 0.66 | 0.54 | 0.55 | 0.75 | 0.75 |
| Al ₂ O ₃ | 10.14 | 10.22 | 7.60 | 7.56 | 6.50 | 6.65 | 10.04 | 10.05 |
| Fe ₂ O ₃ | 1.68 | 1.69 | 2.46 | 2.45 | 2.27 | 2.32 | 1.70 | 1.70 |
| FeO | 2.71 | 2.73 | 2.00 | 1.99 | 1.70 | 1.74 | 3.55 | 3.55 |
| MnO | 0.10 | 0.10 | 0.12 | 0.12 | 0.06 | 0.06 | 0.06 | 0.06 |
| MgO | 2.31 | 2.33 | 2.00 | 1.99 | 2.34 | 2.40 | 2.13 | 2.13 |
| CaO | 0.54 | 0.34 | 0.83 | 0.70 | 1.89 | 0.47 | 0.65 | 0.38 |
| Na ₂ O | 1.88 | 1.90 | 1.28 | 1.27 | 0.85 | 0.87 | 1.98 | 1.98 |
| K ₂ O | 0.56 | 0.56 | 0.78 | 0.78 | 0.85 | 0.87 | 1.08 | 1.08 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.08 | 0.08 | 0.07 | 0.07 | 0.13 | 0.13 |
| H ₂ O+ | 2.43 | 2.45 | 2.18 | 2.17 | 1.84 | 1.88 | 2.30 | 2.30 |
| CO ₂ | 0.16 | 0.00 | 0.10 | 0.00 | 1.13 | 0.00 | 0.21 | 0.00 |
| Total | 99.54 | | 100.67 | | 100.24 | | 100.33 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 220 | | 237 | | 165 | | 295 | |
| ce | 54 | | 39 | | 18 | | 39 | |
| co | 10 | | 8 | | 8 | | 17 | |
| cr | 110 | | 94 | | 460 | | 90 | |
| cu | 10 | | 7 | | 9 | | 20 | |
| ga | 11 | | 7 | | 6 | | 11 | |
| la | 22 | | 17 | | 9 | | 12 | |
| ni | 45 | | 25 | | 81 | | 38 | |
| pb | 15 | | 13 | | 7 | | 11 | |
| rb | 34 | | 22 | | 29 | | 40 | |
| sr | 85 | | 91 | | 61 | | 99 | |
| th | 6 | | 5 | | 3 | | 5 | |
| u | 2 | | 1 | | 2 | | 3 | |
| y | 22 | | 22 | | 15 | | 22 | |
| zn | 76 | | 59 | | 64 | | 78 | |
| zr | 187 | | 129 | | 148 | | 186 | |
| rb | 15 | | 8 | | 8 | | 13 | |

| <i>Sample</i> | 9ne1 | 9ne1* | 10ne1 | 10ne1* | 11ne1 | 11ne1* | 12ne1 | 12ne1* |
|--------------------------------|--------|-------|-------|--------|--------|--------|--------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 67.32 | 75.64 | NA | NA | 76.02 | 75.72 | 76.84 | 76.58 |
| TiO ₂ | 0.69 | 0.78 | NA | NA | 0.75 | 0.75 | 0.75 | 0.75 |
| Al ₂ O ₃ | 8.51 | 9.56 | NA | NA | 10.03 | 9.99 | 9.21 | 9.18 |
| Fe ₂ O ₃ | 1.07 | 1.20 | NA | NA | 2.15 | 2.14 | 1.99 | 1.98 |
| FeO | 3.03 | 3.40 | NA | NA | 2.75 | 2.74 | 2.80 | 2.79 |
| MnO | 0.15 | 0.17 | NA | NA | 0.05 | 0.05 | 0.07 | 0.07 |
| MgO | 1.89 | 2.12 | NA | NA | 2.25 | 2.24 | 2.16 | 2.15 |
| CaO | 7.16 | 0.82 | NA | NA | 1.55 | 1.16 | 0.31 | 0.00 |
| Na ₂ O | 2.57 | 2.89 | NA | NA | 1.72 | 1.71 | 2.42 | 2.41 |
| K ₂ O | 0.99 | 1.11 | NA | NA | 1.11 | 1.11 | 1.32 | 1.32 |
| P ₂ O ₅ | 0.15 | 0.17 | NA | NA | 0.11 | 0.11 | 0.13 | 0.13 |
| H ₂ O+ | 1.90 | 2.13 | NA | NA | 2.29 | 2.28 | 2.58 | 2.57 |
| CO ₂ | 5.06 | 0.00 | NA | NA | 0.30 | 0.00 | 0.30 | 0.06 |
| Total | 100.47 | | NA | | 101.06 | | 100.87 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 225 | | NA | | 280 | | 301 | |
| ce | 30 | | NA | | 58 | | 55 | |
| co | 14 | | NA | | 16 | | 13 | |
| cr | 64 | | NA | | 117 | | 104 | |
| cu | 9 | | NA | | 16 | | 12 | |
| ga | 9 | | NA | | 10 | | 11 | |
| la | 15 | | NA | | 29 | | 29 | |
| ni | 25 | | NA | | 49 | | 39 | |
| pb | 6 | | NA | | 11 | | 13 | |
| rb | 35 | | NA | | 35 | | 43 | |
| sr | 110 | | NA | | 119 | | 101 | |
| th | 5 | | NA | | 5 | | 5 | |
| u | 2 | | NA | | 2 | | 2 | |
| y | 23 | | NA | | 23 | | 25 | |
| zn | 56 | | NA | | 65 | | 59 | |
| zr | 163 | | NA | | 199 | | 219 | |
| nb | 8 | | NA | | 11 | | 11 | |

| <i>Sample</i> | 13ne1 | 13ne1* | 14ne1 | 14ne1* | 15ne1 | 15ne1* | 16ne1 | 16ne1* |
|--------------------------------|--------|--------|--------|--------|-------|--------|-------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 73.92 | 73.56 | 73.71 | 72.76 | 72.57 | 73.17 | 71.88 | 72.61 |
| TiO ₂ | 0.87 | 0.87 | 1.00 | 0.99 | 0.88 | 0.89 | 0.95 | 0.96 |
| Al ₂ O ₃ | 11.55 | 11.49 | 11.52 | 11.37 | 10.82 | 10.91 | 10.95 | 11.06 |
| Fe ₂ O ₃ | 2.82 | 2.81 | 2.23 | 2.20 | 3.74 | 3.77 | 2.51 | 2.54 |
| FeO | 2.56 | 2.55 | 3.14 | 3.10 | 2.26 | 2.28 | 2.89 | 2.92 |
| MnO | 0.04 | 0.04 | 0.05 | 0.05 | 0.07 | 0.07 | 0.16 | 0.16 |
| MgO | 2.45 | 2.44 | 2.81 | 2.77 | 2.73 | 2.75 | 2.87 | 2.90 |
| CaO | 0.57 | 0.39 | 0.60 | 0.59 | 0.32 | 0.25 | 0.30 | 0.20 |
| Na ₂ O | 2.10 | 2.09 | 2.12 | 2.09 | 2.20 | 2.22 | 2.48 | 2.51 |
| K ₂ O | 1.42 | 1.41 | 1.35 | 1.33 | 1.46 | 1.47 | 1.25 | 1.26 |
| P ₂ O ₅ | 0.15 | 0.15 | 0.15 | 0.15 | 0.13 | 0.13 | 0.14 | 0.14 |
| H ₂ O+ | 2.22 | 2.21 | 2.63 | 2.60 | 2.07 | 2.09 | 2.72 | 2.75 |
| CO ₂ | 0.14 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.08 | 0.00 |
| Total | 100.78 | | 101.29 | | 99.29 | | 99.18 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 360 | | 320 | | 304 | | 339 | |
| ce | 43 | | 26 | | 46 | | 44 | |
| co | 13 | | 16 | | 13 | | 17 | |
| cr | 127 | | 168 | | 119 | | 149 | |
| cu | 16 | | 11 | | 15 | | 12 | |
| ga | 12 | | 11 | | 11 | | 14 | |
| la | 18 | | 9 | | 13 | | 15 | |
| ni | 46 | | 46 | | 31 | | 46 | |
| pb | 11 | | 9 | | 13 | | 9 | |
| rb | 43 | | 41 | | 40 | | 42 | |
| sr | 108 | | 83 | | 95 | | 89 | |
| th | 7 | | 8 | | 7 | | 6 | |
| u | 2 | | 3 | | 4 | | 3 | |
| y | 26 | | 24 | | 22 | | 24 | |
| zn | 86 | | 91 | | 74 | | 96 | |
| zr | 227 | | 367 | | 198 | | 236 | |
| rb | 14 | | 16 | | 15 | | 14 | |

| <i>Sample</i> | 17ne1 | 17ne1* | 18ne1 | 18ne1* | 19ne1 | 19ne1* | 20ne1 | 20ne1* |
|--------------------------------|--------|--------|--------|--------|-------|--------|--------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 72.87 | 72.59 | 76.17 | 75.71 | 76.66 | 77.10 | 72.99 | 75.39 |
| TiO ₂ | 0.90 | 0.90 | 0.71 | 0.71 | 0.78 | 0.78 | 0.76 | 0.78 |
| Al ₂ O ₃ | 10.92 | 10.88 | 9.60 | 9.54 | 8.95 | 9.00 | 10.78 | 11.13 |
| Fe ₂ O ₃ | 3.30 | 3.29 | 2.41 | 2.40 | 2.00 | 2.01 | 1.76 | 1.82 |
| FeO | 2.63 | 2.62 | 2.44 | 2.43 | 2.41 | 2.42 | 2.25 | 2.32 |
| MnO | 0.04 | 0.04 | 0.08 | 0.08 | 0.10 | 0.10 | 0.13 | 0.13 |
| MgO | 2.94 | 2.93 | 2.41 | 2.40 | 2.47 | 2.48 | 1.95 | 2.01 |
| CaO | 0.29 | 0.16 | 0.76 | 0.67 | 0.89 | 0.74 | 2.73 | 0.58 |
| Na ₂ O | 2.21 | 2.20 | 2.19 | 2.18 | 2.23 | 2.24 | 2.56 | 2.64 |
| K ₂ O | 1.44 | 1.43 | 1.31 | 1.30 | 1.25 | 1.26 | 1.10 | 1.14 |
| P ₂ O ₅ | 0.14 | 0.14 | 0.13 | 0.13 | 0.10 | 0.10 | 0.18 | 0.19 |
| H ₂ O+ | 2.83 | 2.82 | 2.49 | 2.47 | 1.74 | 1.75 | 1.80 | 1.86 |
| CO ₂ | 0.10 | 0.00 | 0.07 | 0.00 | 0.12 | 0.00 | 1.71 | 0.00 |
| Total | 100.61 | | 100.77 | | 99.70 | | 100.67 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 374 | | 374 | | 299 | | 260 | |
| ce | 27 | | 40 | | 36 | | 38 | |
| co | 17 | | 10 | | 9 | | 12 | |
| cr | 108 | | 98 | | 134 | | 154 | |
| cu | 9 | | 11 | | 12 | | 11 | |
| ga | 11 | | 9 | | 9 | | 10 | |
| la | 14 | | 19 | | 12 | | 18 | |
| ni | 47 | | 43 | | 45 | | 43 | |
| pb | 12 | | 11 | | 11 | | 8 | |
| rb | 47 | | 41 | | 36 | | 37 | |
| sr | 79 | | 103 | | 81 | | 107 | |
| th | 6 | | 7 | | 5 | | 6 | |
| u | 4 | | 2 | | 2 | | 2 | |
| y | 23 | | 21 | | 23 | | 29 | |
| zn | 94 | | 82 | | 79 | | 70 | |
| zr | 188 | | 160 | | 177 | | 202 | |
| rb | 13 | | 12 | | 13 | | 15 | |

| <i>Sample</i> | 21ne1 | 21ne1* | 22ne1 | 22ne1* | 23ne1 | 23ne1* | 24ne1 | 24ne1* |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.66 | 80.15 | 70.10 | 69.59 | 72.56 | 71.65 | 73.06 | 72.66 |
| TiO ₂ | 0.60 | 0.60 | 1.03 | 1.02 | 0.83 | 0.82 | 0.92 | 0.92 |
| Al ₂ O ₃ | 7.56 | 7.51 | 12.13 | 12.04 | 11.69 | 11.54 | 10.74 | 10.68 |
| Fe ₂ O ₃ | 2.18 | 2.17 | 3.02 | 3.00 | 2.15 | 2.12 | 2.89 | 2.87 |
| FeO | 1.55 | 1.54 | 3.19 | 3.17 | 3.48 | 3.44 | 3.00 | 2.98 |
| MnO | 0.07 | 0.07 | 0.06 | 0.06 | 0.08 | 0.08 | 0.07 | 0.07 |
| MgO | 2.84 | 2.82 | 3.41 | 3.39 | 3.44 | 3.40 | 3.72 | 3.70 |
| CaO | 0.46 | 0.28 | 0.83 | 0.70 | 0.53 | 0.47 | 0.96 | 0.55 |
| Na ₂ O | 1.53 | 1.52 | 3.10 | 3.08 | 2.72 | 2.69 | 2.29 | 2.28 |
| K ₂ O | 1.25 | 1.24 | 1.21 | 1.20 | 1.00 | 0.99 | 0.73 | 0.73 |
| P ₂ O ₅ | 0.09 | 0.09 | 0.17 | 0.17 | 0.13 | 0.13 | 0.12 | 0.12 |
| H ₂ O+ | 2.03 | 2.02 | 2.61 | 2.59 | 2.71 | 2.68 | 2.45 | 2.44 |
| CO ₂ | 0.14 | 0.00 | 0.10 | 0.00 | 0.04 | 0.00 | 0.32 | 0.00 |
| Total | 100.96 | | 100.92 | | 101.35 | | 101.23 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 264 | | 339 | | 233 | | 212 | |
| ce | 21 | | 45 | | 18 | | 33 | |
| co | 8 | | 23 | | 19 | | 20 | |
| cr | 590 | | 154 | | 113 | | 232 | |
| cu | 12 | | 9 | | 9 | | 11 | |
| ga | 8 | | 13 | | 13 | | 12 | |
| la | 12 | | 15 | | 10 | | 13 | |
| ni | 91 | | 54 | | 58 | | 55 | |
| pb | 10 | | 12 | | 8 | | 11 | |
| rb | 39 | | 42 | | 36 | | 25 | |
| sr | 58 | | 192 | | 154 | | 161 | |
| th | 6 | | 9 | | 8 | | 7 | |
| u | 2 | | 2 | | 3 | | 4 | |
| y | 18 | | 28 | | 20 | | 24 | |
| zn | 78 | | 117 | | 113 | | 112 | |
| zr | 166 | | 357 | | 188 | | 270 | |
| rb | 11 | | 18 | | 14 | | 6 | |

| <i>Sample</i> | 25ne1 | 25ne1* | 1ne2 | 1ne2* | 2ne2 | 2ne2* | 3ne2 | 3ne2* |
|--------------------------------|--------|--------|--------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 71.28 | 70.63 | 71.67 | 71.52 | 75.56 | 76.74 | 81.16 | 81.18 |
| TiO ₂ | 0.90 | 0.89 | 0.91 | 0.91 | 0.63 | 0.64 | 0.51 | 0.51 |
| Al ₂ O ₃ | 11.53 | 11.42 | 11.32 | 11.30 | 9.51 | 9.66 | 7.94 | 7.94 |
| Fe ₂ O ₃ | 2.90 | 2.87 | 2.95 | 2.94 | 1.47 | 1.49 | 1.36 | 1.36 |
| FeO | 3.10 | 3.07 | 3.14 | 3.13 | 2.56 | 2.60 | 2.15 | 2.15 |
| MnO | 0.07 | 0.07 | 0.00 | 0.00 | 0.08 | 0.08 | 0.06 | 0.06 |
| MgO | 3.78 | 3.75 | 3.09 | 3.08 | 2.61 | 2.65 | 1.58 | 1.58 |
| CaO | 1.00 | 0.88 | 0.30 | 0.26 | 1.62 | 0.24 | 0.15 | 0.00 |
| Na ₂ O | 2.70 | 2.68 | 2.35 | 2.35 | 2.19 | 2.22 | 2.20 | 2.20 |
| K ₂ O | 0.88 | 0.87 | 1.51 | 1.51 | 1.18 | 1.20 | 1.03 | 1.03 |
| P ₂ O ₅ | 0.12 | 0.12 | 0.15 | 0.15 | 0.09 | 0.09 | 0.07 | 0.07 |
| H ₂ O+ | 2.78 | 2.75 | 2.86 | 2.85 | 2.35 | 2.39 | 1.89 | 1.89 |
| CO ₂ | 0.09 | 0.00 | 0.03 | 0.00 | 1.09 | 0.00 | 0.12 | 0.03 |
| Total | 101.11 | | 100.28 | | 100.94 | | 100.22 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 249 | | 276 | | 153 | | 209 | |
| ce | 43 | | 23 | | 43 | | 18 | |
| co | 19 | | 17 | | 13 | | 11 | |
| cr | 130 | | 112 | | 148 | | 48 | |
| cu | 9 | | 11 | | 4 | | 7 | |
| ga | 14 | | 14 | | 10 | | 9 | |
| la | 18 | | 8 | | 20 | | 7 | |
| ni | 55 | | 60 | | 32 | | 28 | |
| pb | 10 | | 18 | | 10 | | 8 | |
| rb | 29 | | 48 | | 45 | | 35 | |
| sr | 206 | | 90 | | 77 | | 85 | |
| th | 7 | | 9 | | 7 | | 4 | |
| u | 2 | | 2 | | 3 | | 3 | |
| y | 26 | | 21 | | 26 | | 14 | |
| zn | 117 | | 95 | | 75 | | 57 | |
| zr | 233 | | 196 | | 211 | | 119 | |
| nb | 16 | | 15 | | 11 | | 10 | |

| <i>Sample</i> | 4ne2 | 4ne2* | 5ne2 | 5ne2* | 6ne2 | 6ne2* | 7ne2 | 7ne2* |
|--------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 76.67 | 76.59 | 77.74 | 77.84 | 79.03 | 79.14 | 77.81 | 77.35 |
| TiO ₂ | 0.80 | 0.80 | 0.80 | 0.80 | 0.76 | 0.76 | 0.87 | 0.86 |
| Al ₂ O ₃ | 9.15 | 9.14 | 9.11 | 9.12 | 7.88 | 7.89 | 9.46 | 9.40 |
| Fe ₂ O ₃ | 2.06 | 2.06 | 1.75 | 1.75 | 1.80 | 1.80 | 1.69 | 1.68 |
| FeO | 2.65 | 2.65 | 2.59 | 2.59 | 2.72 | 2.72 | 2.91 | 2.89 |
| MnO | 0.07 | 0.07 | 0.06 | 0.06 | 0.08 | 0.08 | 0.07 | 0.07 |
| MgO | 2.49 | 2.49 | 2.63 | 2.63 | 2.34 | 2.34 | 2.28 | 2.27 |
| CaO | 0.21 | 0.03 | 0.19 | 0.13 | 0.43 | 0.19 | 0.18 | 0.00 |
| Na ₂ O | 2.52 | 2.52 | 2.00 | 2.00 | 1.73 | 1.73 | 1.84 | 1.83 |
| K ₂ O | 1.33 | 1.33 | 0.84 | 0.84 | 1.00 | 1.00 | 1.26 | 1.25 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.06 | 0.06 | 0.09 | 0.09 | 0.11 | 0.11 |
| H ₂ O+ | 2.22 | 2.22 | 2.17 | 2.17 | 2.24 | 2.24 | 2.29 | 2.28 |
| CO ₂ | 0.14 | 0.00 | 0.05 | 0.00 | 0.19 | 0.00 | 0.14 | 0.00 |
| Total | 100.42 | | 99.99 | | 100.29 | | 100.91 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 259 | | 170 | | 234 | | 259 | |
| ce | 34 | | 27 | | 35 | | 26 | |
| co | 19 | | 17 | | 12 | | 15 | |
| cr | 87 | | 127 | | 91 | | 82 | |
| cu | 8 | | 9 | | 5 | | 5 | |
| ga | 12 | | 10 | | 9 | | 9 | |
| la | 10 | | 8 | | 17 | | 0 | |
| ni | 37 | | 44 | | 34 | | 35 | |
| pb | 12 | | 10 | | 14 | | 15 | |
| rb | 44 | | 29 | | 31 | | 41 | |
| sr | 75 | | 77 | | 70 | | 63 | |
| th | 7 | | 5 | | 7 | | 7 | |
| u | 3 | | 2 | | 4 | | 3 | |
| y | 21 | | 19 | | 23 | | 21 | |
| zn | 76 | | 76 | | 73 | | 73 | |
| zr | 203 | | 202 | | 187 | | 228 | |
| rb | 16 | | 10 | | 11 | | 14 | |

| <i>Sample</i> | 8ne2 | 8ne2* | 9ne2 | 9ne2* | 10ne2 | 10ne2* | 11ne2 | 11ne2* |
|--------------------------------|--------|-------|--------|-------|-------|--------|--------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 79.21 | 79.04 | 74.73 | 74.33 | 80.24 | 80.53 | 73.28 | 75.79 |
| TiO ₂ | 0.39 | 0.39 | 0.90 | 0.90 | 0.67 | 0.67 | 0.91 | 0.94 |
| Al ₂ O ₃ | 9.85 | 9.83 | 10.70 | 10.64 | 7.47 | 7.50 | 10.12 | 10.47 |
| Fe ₂ O ₃ | 0.84 | 0.84 | 1.98 | 1.97 | 1.97 | 1.98 | 1.74 | 1.80 |
| FeO | 1.90 | 1.90 | 3.51 | 3.49 | 2.40 | 2.41 | 3.26 | 3.37 |
| MnO | 0.06 | 0.06 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| MgO | 1.41 | 1.41 | 2.64 | 2.63 | 2.12 | 2.13 | 2.33 | 2.41 |
| CaO | 0.32 | 0.07 | 0.34 | 0.16 | 0.28 | 0.18 | 1.41 | 0.00 |
| Na ₂ O | 3.39 | 3.38 | 1.70 | 1.69 | 1.52 | 1.53 | 1.97 | 2.04 |
| K ₂ O | 1.37 | 1.37 | 1.35 | 1.34 | 1.01 | 1.01 | 1.41 | 1.46 |
| P ₂ O ₅ | 0.07 | 0.07 | 0.11 | 0.11 | 0.08 | 0.08 | 0.12 | 0.12 |
| H ₂ O+ | 1.66 | 1.66 | 2.67 | 2.66 | 1.90 | 1.91 | 0.91 | 0.94 |
| CO ₂ | 0.20 | 0.00 | 0.14 | 0.00 | 0.08 | 0.00 | 2.64 | 0.57 |
| Total | 100.67 | | 100.85 | | 99.82 | | 100.18 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 318 | | 321 | | 206 | | 269 | |
| ce | 29 | | 31 | | 31 | | 26 | |
| co | 3 | | 16 | | 11 | | 16 | |
| cr | 33 | | 106 | | 95 | | 84 | |
| cu | 6 | | 8 | | 7 | | 6 | |
| ga | 8 | | 10 | | 9 | | 13 | |
| la | 10 | | 15 | | 12 | | 12 | |
| ni | 10 | | 36 | | 34 | | 35 | |
| pb | 8 | | 11 | | 12 | | 11 | |
| rb | 32 | | 45 | | 32 | | 46 | |
| sr | 132 | | 65 | | 50 | | 64 | |
| th | 6 | | 8 | | 6 | | 7 | |
| u | 2 | | 3 | | 2 | | 1 | |
| y | 15 | | 27 | | 20 | | 24 | |
| zn | 58 | | 82 | | 63 | | 78 | |
| zr | 109 | | 220 | | 146 | | 225 | |
| rb | 10 | | 13 | | 7 | | 12 | |

| <i>Sample</i> | 12ne2 | 12ne2* | 13ne2 | 13ne2* | 14ne2 | 14ne2* | 15ne2 | 15ne2* |
|--------------------------------|--------|--------|-------|--------|-------|--------|-------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 76.74 | 76.58 | 74.48 | 75.18 | 77.54 | 77.84 | 76.75 | 77.25 |
| TiO ₂ | 0.72 | 0.72 | 0.55 | 0.56 | 0.77 | 0.77 | 0.89 | 0.90 |
| Al ₂ O ₃ | 8.98 | 8.96 | 8.77 | 8.85 | 8.35 | 8.38 | 9.05 | 9.11 |
| Fe ₂ O ₃ | 2.29 | 2.29 | 3.12 | 3.15 | 2.26 | 2.27 | 2.07 | 2.08 |
| FeO | 2.38 | 2.38 | 2.76 | 2.79 | 2.19 | 2.20 | 3.08 | 3.10 |
| MnO | 0.07 | 0.07 | 0.06 | 0.06 | 0.08 | 0.08 | 0.06 | 0.06 |
| MgO | 2.97 | 2.96 | 3.27 | 3.30 | 2.93 | 2.94 | 2.01 | 2.02 |
| CaO | 0.16 | 0.01 | 0.45 | 0.06 | 0.23 | 0.14 | 0.41 | 0.22 |
| Na ₂ O | 1.93 | 1.93 | 2.26 | 2.28 | 1.65 | 1.66 | 1.63 | 1.64 |
| K ₂ O | 1.36 | 1.36 | 0.64 | 0.65 | 1.14 | 1.14 | 1.10 | 1.11 |
| P ₂ O ₅ | 0.11 | 0.11 | 0.09 | 0.09 | 0.13 | 0.13 | 0.11 | 0.11 |
| H ₂ O+ | 2.65 | 2.64 | 3.01 | 3.04 | 2.43 | 2.44 | 2.38 | 2.40 |
| CO ₂ | 0.12 | 0.00 | 0.31 | 0.00 | 0.07 | 0.00 | 0.15 | 0.00 |
| Total | 100.48 | | 99.77 | | 99.77 | | 99.69 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 206 | | 131 | | 201 | | 246 | |
| ce | 35 | | 18 | | 19 | | 24 | |
| co | 15 | | 18 | | 20 | | 13 | |
| cr | 353 | | 141 | | 597 | | 106 | |
| cu | 6 | | 9 | | 12 | | 9 | |
| ga | 9 | | 8 | | 8 | | 10 | |
| la | 15 | | 2 | | 12 | | 10 | |
| ni | 95 | | 60 | | 84 | | 38 | |
| pb | 9 | | 11 | | 10 | | 10 | |
| rb | 46 | | 23 | | 38 | | 36 | |
| sr | 60 | | 69 | | 59 | | 59 | |
| th | 7 | | 6 | | 6 | | 8 | |
| u | 3 | | 2 | | 3 | | 2 | |
| y | 17 | | 15 | | 25 | | 22 | |
| zn | 75 | | 84 | | 91 | | 75 | |
| zr | 198 | | 101 | | 180 | | 253 | |
| nb | 9 | | 7 | | 10 | | 16 | |

| <i>Sample</i> | 16ne2 | 16ne2* | 17ne2 | 17ne2* | 18ne2 | 18ne2* | 19ne2 | 19ne2* |
|--------------------------------|-------|--------|-------|--------|--------|--------|--------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 81.93 | 82.11 | 75.07 | 75.65 | 77.37 | 76.83 | 73.94 | 73.91 |
| TiO ₂ | 0.56 | 0.56 | 0.92 | 0.93 | 0.65 | 0.65 | 0.75 | 0.75 |
| Al ₂ O ₃ | 6.72 | 6.74 | 10.17 | 10.25 | 9.25 | 9.18 | 10.15 | 10.15 |
| Fe ₂ O ₃ | 2.32 | 2.33 | 1.61 | 1.62 | 1.75 | 1.74 | 2.09 | 2.09 |
| FeO | 1.99 | 1.99 | 3.22 | 3.24 | 2.36 | 2.34 | 2.69 | 2.69 |
| MnO | 0.07 | 0.07 | 0.06 | 0.06 | 0.06 | 0.06 | 0.07 | 0.07 |
| MgO | 2.07 | 2.07 | 2.32 | 2.34 | 2.86 | 2.84 | 3.42 | 3.42 |
| CaO | 0.10 | 0.00 | 0.13 | 0.00 | 0.12 | 0.07 | 0.25 | 0.14 |
| Na ₂ O | 1.05 | 1.05 | 1.69 | 1.70 | 2.07 | 2.06 | 2.02 | 2.02 |
| K ₂ O | 0.67 | 0.67 | 1.39 | 1.40 | 1.55 | 1.54 | 1.65 | 1.65 |
| P ₂ O ₅ | 0.06 | 0.06 | 0.12 | 0.12 | 0.11 | 0.11 | 0.12 | 0.12 |
| H ₂ O+ | 2.32 | 2.33 | 2.64 | 2.66 | 2.61 | 2.59 | 3.01 | 3.01 |
| CO ₂ | 0.08 | 0.02 | 0.14 | 0.03 | 0.04 | 0.00 | 0.09 | 0.00 |
| Total | 99.94 | | 99.48 | | 100.80 | | 100.25 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 133 | | 266 | | 199 | | 210 | |
| ce | 24 | | 32 | | 31 | | 26 | |
| co | 15 | | 12 | | 12 | | 18 | |
| cr | 99 | | 91 | | 294 | | 326 | |
| cu | 8 | | 5 | | 9 | | 11 | |
| ga | 7 | | 10 | | 9 | | 10 | |
| la | 8 | | 28 | | 12 | | 10 | |
| ni | 32 | | 38 | | 93 | | 94 | |
| pb | 10 | | 13 | | 12 | | 11 | |
| rb | 19 | | 45 | | 50 | | 53 | |
| sr | 39 | | 56 | | 56 | | 56 | |
| th | 5 | | 6 | | 9 | | 7 | |
| u | 2 | | 3 | | 3 | | 2 | |
| y | 16 | | 22 | | 17 | | 20 | |
| zn | 69 | | 78 | | 77 | | 86 | |
| zr | 97 | | 256 | | 170 | | 200 | |
| nb | 7 | | 13 | | 14 | | 14 | |

| <i>Sample</i> | 20ne2 | 20ne2* | 21ne2 | 21ne2* | 22ne2 | 22ne2* | 23ne2 | 23ne2* |
|--------------------------------|-------|--------|--------|--------|-------|--------|-------|--------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 80.72 | 81.59 | 80.87 | 80.62 | 68.83 | 73.76 | 73.32 | 74.50 |
| TiO ₂ | 0.56 | 0.57 | 0.67 | 0.67 | 0.85 | 0.91 | 0.86 | 0.87 |
| Al ₂ O ₃ | 7.08 | 7.16 | 7.69 | 7.67 | 9.87 | 10.58 | 10.53 | 10.70 |
| Fe ₂ O ₃ | 2.03 | 2.05 | 1.87 | 1.86 | 3.20 | 3.43 | 1.92 | 1.95 |
| FeO | 1.79 | 1.81 | 2.40 | 2.39 | 2.49 | 2.67 | 2.75 | 2.79 |
| MnO | 0.06 | 0.06 | 0.08 | 0.08 | 0.12 | 0.13 | 0.08 | 0.08 |
| MgO | 3.00 | 3.03 | 2.35 | 2.34 | 2.60 | 2.79 | 2.58 | 2.62 |
| CaO | 0.46 | 0.12 | 0.42 | 0.20 | 3.80 | 0.33 | 0.91 | 0.27 |
| Na ₂ O | 0.42 | 0.42 | 0.43 | 0.43 | 1.17 | 1.25 | 1.89 | 1.92 |
| K ₂ O | 0.96 | 0.97 | 1.04 | 1.04 | 1.12 | 1.20 | 1.30 | 1.32 |
| P ₂ O ₅ | 0.08 | 0.08 | 0.07 | 0.07 | 0.11 | 0.12 | 0.11 | 0.11 |
| H ₂ O+ | 2.12 | 2.14 | 2.64 | 2.63 | 2.65 | 2.84 | 2.81 | 2.86 |
| CO ₂ | 0.27 | 0.00 | 0.17 | 0.00 | 2.75 | 0.00 | 0.51 | 0.00 |
| Total | 99.54 | | 100.68 | | 99.56 | | 99.54 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 151 | | 195 | | 1037 | | 287 | |
| ce | 25 | | 24 | | 63 | | 42 | |
| co | 16 | | 14 | | 15 | | 14 | |
| cr | 679 | | 110 | | 113 | | 129 | |
| cu | 11 | | 6 | | 12 | | 11 | |
| ga | 8 | | 9 | | 10 | | 11 | |
| la | 14 | | 7 | | 28 | | 14 | |
| ni | 97 | | 34 | | 45 | | 43 | |
| pb | 11 | | 14 | | 13 | | 16 | |
| rb | 33 | | 31 | | 39 | | 41 | |
| sr | 44 | | 37 | | 98 | | 82 | |
| th | 6 | | 5 | | 7 | | 8 | |
| u | 3 | | 2 | | 3 | | 3 | |
| y | 15 | | 18 | | 30 | | 16 | |
| zn | 81 | | 73 | | 88 | | 82 | |
| zr | 177 | | 142 | | 215 | | 207 | |
| nb | 7 | | 7 | | 10 | | 11 | |

| <i>Sample</i> | 24ne2 | 24ne2* | 25ne2 | 25ne2* | 26ne2 | 26ne2* | 1ne3 | 1ne3* |
|--------------------------------|-------|--------|-------|--------|-------|--------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 75.06 | 75.92 | 70.39 | 70.72 | 72.27 | 72.47 | 74.91 | 74.57 |
| TiO ₂ | 0.82 | 0.83 | 0.99 | 0.99 | 0.97 | 0.97 | 0.46 | 0.46 |
| Al ₂ O ₃ | 9.81 | 9.92 | 12.29 | 12.35 | 11.29 | 11.32 | 11.75 | 11.70 |
| Fe ₂ O ₃ | 1.70 | 1.72 | 2.15 | 2.16 | 1.99 | 2.00 | 2.11 | 2.10 |
| FeO | 2.91 | 2.94 | 2.97 | 2.98 | 3.16 | 3.17 | 1.94 | 1.93 |
| MnO | 0.09 | 0.09 | 0.10 | 0.10 | 0.07 | 0.07 | 0.06 | 0.06 |
| MgO | 2.64 | 2.67 | 3.59 | 3.61 | 3.22 | 3.23 | 1.93 | 1.92 |
| CaO | 0.81 | 0.70 | 0.29 | 0.21 | 0.29 | 0.29 | 0.19 | 0.02 |
| Na ₂ O | 1.74 | 1.76 | 2.05 | 2.06 | 1.96 | 1.97 | 3.13 | 3.12 |
| K ₂ O | 1.04 | 1.05 | 1.18 | 1.19 | 1.07 | 1.07 | 1.95 | 1.94 |
| P ₂ O ₅ | 0.00 | 0.00 | 0.13 | 0.13 | 0.15 | 0.15 | 0.08 | 0.08 |
| H ₂ O+ | 2.36 | 2.39 | 3.48 | 3.50 | 3.28 | 3.29 | 2.11 | 2.10 |
| CO ₂ | 0.09 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 |
| Total | 99.04 | | 99.65 | | 99.69 | | 100.73 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| | 323 | 533 | 864 | 532 | | | | |
| ce | 41 | 35 | 46 | 24 | | | | |
| co | 19 | 12 | 11 | 10 | | | | |
| cr | 117 | 118 | 127 | 56 | | | | |
| cu | 29 | 44 | 87 | 11 | | | | |
| ga | 12 | 15 | 13 | 11 | | | | |
| la | 29 | 7 | 17 | 7 | | | | |
| ni | 49 | 57 | 57 | 21 | | | | |
| pb | 12 | 18 | 21 | 11 | | | | |
| rb | 35 | 42 | 37 | 56 | | | | |
| sr | 93 | 156 | 176 | 146 | | | | |
| th | 6 | 8 | 8 | 7 | | | | |
| u | 3 | 3 | 3 | 2 | | | | |
| y | 35 | 30 | 29 | 17 | | | | |
| zn | 93 | 97 | 82 | 69 | | | | |
| zr | 184 | 212 | 258 | 130 | | | | |
| nb | 11 | 18 | 16 | 4 | | | | |

| <i>Sample</i> | 2ne3 | 2ne3* | 3ne3 | 3ne3* | 1ne4 | 1ne4* | 2ne4 | 2ne4* |
|--------------------------------|-------|-------|-------|-------|--------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 74.53 | 74.73 | 82.98 | 83.61 | 43.34 | 68.36 | 72.27 | 76.04 |
| TiO ₂ | 0.49 | 0.49 | 0.44 | 0.44 | 0.61 | 0.96 | 0.55 | 0.58 |
| Al ₂ O ₃ | 11.82 | 11.85 | 6.44 | 6.49 | 7.54 | 11.89 | 10.33 | 10.87 |
| Fe ₂ O ₃ | 1.50 | 1.50 | 1.37 | 1.38 | 1.58 | 2.49 | 1.29 | 1.36 |
| FeO | 1.94 | 1.95 | 1.68 | 1.69 | 2.39 | 3.77 | 2.31 | 2.43 |
| MnO | 0.07 | 0.07 | 0.04 | 0.04 | 0.36 | 0.57 | 0.07 | 0.07 |
| MgO | 1.81 | 1.81 | 2.40 | 2.42 | 2.10 | 3.31 | 2.11 | 2.22 |
| CaO | 0.13 | 0.07 | 0.13 | 0.00 | 21.70 | 1.78 | 3.08 | 0.00 |
| Na ₂ O | 2.69 | 2.70 | 0.71 | 0.72 | 1.14 | 1.80 | 2.18 | 2.29 |
| K ₂ O | 2.56 | 2.57 | 1.06 | 1.07 | 0.88 | 1.39 | 1.11 | 1.17 |
| P ₂ O ₅ | 0.08 | 0.08 | 0.06 | 0.06 | 0.14 | 0.22 | 0.13 | 0.14 |
| H ₂ O+ | 2.17 | 2.18 | 2.04 | 2.06 | 2.19 | 3.45 | 2.16 | 2.27 |
| CO ₂ | 0.05 | 0.00 | 0.13 | 0.03 | 16.20 | 0.00 | 2.53 | 0.56 |
| Total | 99.80 | | 99.46 | | 100.15 | | 100.09 | |

| | | | | | | | | |
|--------------------------------|-----|--|-----|--|-----|--|-----|--|
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 590 | | 225 | | 242 | | 247 | |
| ce | 19 | | 27 | | 35 | | 48 | |
| co | 9 | | 9 | | 8 | | 11 | |
| cr | 46 | | 486 | | 97 | | 76 | |
| cu | 7 | | 9 | | 9 | | 14 | |
| ga | 10 | | 7 | | 9 | | 11 | |
| la | 5 | | 14 | | 9 | | 17 | |
| ni | 18 | | 82 | | 41 | | 47 | |
| pb | 4 | | 9 | | 4 | | 7 | |
| rb | 67 | | 34 | | 31 | | 42 | |
| sr | 105 | | 42 | | 311 | | 136 | |
| th | 7 | | 7 | | 6 | | 7 | |
| u | 3 | | 3 | | 2 | | 2 | |
| y | 14 | | 15 | | 21 | | 16 | |
| zn | 71 | | 66 | | 56 | | 52 | |
| zr | 142 | | 149 | | 161 | | 148 | |
| nb | 10 | | 6 | | 10 | | 10 | |

| <i>Sample</i> | 3ne4 | 3ne4* | 4ne4 | 4ne4* | 5ne4 | 5ne4* | 6ne4 | 6ne4* |
|--------------------------------|--------|-------|--------|-------|-------|-------|--------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 75.10 | 79.47 | 78.21 | 77.81 | 75.77 | 76.36 | 76.10 | 76.14 |
| TiO ₂ | 0.41 | 0.43 | 0.69 | 0.69 | 1.03 | 1.04 | 0.88 | 0.88 |
| Al ₂ O ₃ | 8.72 | 9.23 | 9.47 | 9.42 | 9.82 | 9.90 | 9.95 | 9.96 |
| Fe ₂ O ₃ | 1.00 | 1.06 | 1.08 | 1.07 | 1.73 | 1.74 | 1.57 | 1.57 |
| FeO | 1.90 | 2.01 | 3.40 | 3.38 | 2.95 | 2.97 | 3.29 | 3.29 |
| MnO | 0.06 | 0.06 | 0.08 | 0.08 | 0.06 | 0.06 | 0.07 | 0.07 |
| MgO | 2.14 | 2.26 | 2.26 | 2.25 | 2.27 | 2.29 | 2.28 | 2.28 |
| CaO | 3.35 | 0.28 | 0.10 | 0.00 | 0.13 | 0.00 | 0.18 | 0.00 |
| Na ₂ O | 2.29 | 2.42 | 1.85 | 1.84 | 1.79 | 1.80 | 1.67 | 1.67 |
| K ₂ O | 0.82 | 0.87 | 0.93 | 0.93 | 1.09 | 1.10 | 1.33 | 1.33 |
| P ₂ O ₅ | 0.00 | 0.00 | 0.10 | 0.10 | 0.12 | 0.12 | 0.12 | 0.12 |
| H ₂ O+ | 1.80 | 1.90 | 2.42 | 2.41 | 2.57 | 2.59 | 2.65 | 2.65 |
| CO ₂ | 2.43 | 0.00 | 0.10 | 0.02 | 0.12 | 0.03 | 0.15 | 0.03 |
| Total | 100.00 | | 100.68 | | 99.43 | | 100.22 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 184 | | 164 | | 228 | | 302 | |
| ce | 34 | | 25 | | 39 | | 20 | |
| co | 9 | | 13 | | 12 | | 17 | |
| cr | 162 | | 120 | | 124 | | 94 | |
| cu | 17 | | 6 | | 6 | | 8 | |
| ga | 9 | | 9 | | 11 | | 11 | |
| la | 16 | | 7 | | 18 | | 2 | |
| ni | 49 | | 44 | | 38 | | 34 | |
| pb | 7 | | 7 | | 9 | | 7 | |
| rb | 25 | | 33 | | 40 | | 46 | |
| sr | 98 | | 63 | | 61 | | 73 | |
| th | 7 | | 6 | | 7 | | 7 | |
| u | 2 | | 1 | | 4 | | 3 | |
| y | 20 | | 15 | | 29 | | 20 | |
| zn | 57 | | 78 | | 85 | | 80 | |
| zr | 124 | | 136 | | 284 | | 225 | |
| rb | 7 | | 12 | | 15 | | 12 | |

| <i>Sample</i> | 7ne4 | 7ne4 | 8ne4 | 8ne4 | 1ne5 | 1ne5* | 2ne5 | 2ne5* |
|--------------------------------|--------|-------|--------|-------|-------|-------|-------|-------|
| <i>chemical analyses (%)</i> | | | | | | | | |
| SiO ₂ | 82.62 | 82.47 | 72.55 | 72.54 | 79.32 | 83.51 | 75.11 | 77.11 |
| TiO ₂ | 0.48 | 0.48 | 0.98 | 0.98 | 0.65 | 0.68 | 0.76 | 0.78 |
| Al ₂ O ₃ | 7.09 | 7.08 | 9.95 | 9.95 | 5.97 | 6.29 | 8.85 | 9.09 |
| Fe ₂ O ₃ | 1.23 | 1.23 | 3.23 | 3.23 | 1.06 | 1.12 | 1.68 | 1.72 |
| FeO | 1.83 | 1.83 | 3.47 | 3.47 | 2.41 | 2.54 | 3.55 | 3.64 |
| MnO | 0.05 | 0.05 | 0.04 | 0.04 | 0.09 | 0.09 | 0.08 | 0.08 |
| MgO | 2.35 | 2.35 | 3.26 | 3.26 | 1.63 | 1.72 | 2.18 | 2.24 |
| CaO | 0.17 | 0.00 | 0.32 | 0.17 | 2.58 | 0.10 | 0.91 | 0.00 |
| Na ₂ O | 1.50 | 1.50 | 2.52 | 2.52 | 0.19 | 0.20 | 0.09 | 0.09 |
| K ₂ O | 0.94 | 0.94 | 0.91 | 0.91 | 0.66 | 0.69 | 0.91 | 0.93 |
| P ₂ O ₅ | 0.08 | 0.08 | 0.19 | 0.19 | 0.08 | 0.08 | 0.10 | 0.10 |
| H ₂ O+ | 2.01 | 2.01 | 2.74 | 2.74 | 2.83 | 2.98 | 3.87 | 3.97 |
| CO ₂ | 0.13 | 0.00 | 0.12 | 0.00 | 1.96 | 0.00 | 1.08 | 0.23 |
| Total | 100.47 | | 100.27 | | 99.43 | | 99.17 | |
| <i>trace elements (p.p.m.)</i> | | | | | | | | |
| ba | 175 | | 247 | | 641 | | 219 | |
| ce | 22 | | 39 | | 54 | | 36 | |
| co | 11 | | 27 | | 45 | | 19 | |
| cr | 238 | | 100 | | 28 | | 82 | |
| cu | 5 | | 16 | | 5 | | 7 | |
| ga | 8 | | 12 | | 8 | | 13 | |
| la | 7 | | 12 | | 27 | | 18 | |
| ni | 82 | | 31 | | 36 | | 63 | |
| pb | 6 | | 15 | | 6 | | 5 | |
| rb | 29 | | 20 | | 22 | | 30 | |
| sr | 52 | | 119 | | 35 | | 26 | |
| th | 5 | | 8 | | 7 | | 4 | |
| u | 3 | | 3 | | 3 | | 2 | |
| y | 13 | | 30 | | 27 | | 21 | |
| zn | 69 | | 109 | | 46 | | 68 | |
| zr | 137 | | 150 | | 395 | | 208 | |
| nb | 8 | | 13 | | 6 | | 7 | |

Sample 3ne5 3ne5*

chemical analyses (%)

| | | |
|--------------------------------|-------|-------|
| SiO ₂ | 72.75 | 74.13 |
| TiO ₂ | 0.90 | 0.92 |
| Al ₂ O ₃ | 10.80 | 11.00 |
| Fe ₂ O ₃ | 2.96 | 3.02 |
| FeO | 2.60 | 2.65 |
| MnO | 0.08 | 0.08 |
| MgO | 2.01 | 2.05 |
| CaO | 0.73 | 0.25 |
| Na ₂ O | 0.49 | 0.50 |
| K ₂ O | 1.42 | 1.45 |
| P ₂ O ₅ | 0.13 | 0.13 |
| H ₂ O+ | 3.75 | 3.82 |
| CO ₂ | 0.38 | 0.00 |
| Total | 99.00 | |

trace elements (p.p.m.)

| | |
|----|-----|
| ba | 317 |
| ce | 53 |
| co | 18 |
| cr | 90 |
| cu | 7 |
| ga | 15 |
| la | 26 |
| ni | 42 |
| pb | 8 |
| rb | 49 |
| sr | 33 |
| th | 7 |
| u | 2 |
| y | 26 |
| zn | 69 |
| zr | 266 |
| nb | 10 |

